Corrosive sulphur in transformers

by

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Abstract

Failures in power transformers, in the majority of cases, have been linked to the formation of copper sulphide (Cu_2S) and corrosive sulphur. Cu_2S is conductive and affects the dielectric properties of the insulation system in the transformer. The formation of Cu_2S and corrosive sulphur in transformers is of worldwide concern to power utility companies, like Eskom, and large industrial manufacturing plants that maintain their own transformers.

This research deals with determining and understanding the formation mechanism of Cu_2S as well as investigating factors that influence the acceleration of the corrosive sulphur formation. Data from oil test results was obtained from an experimental set-up belonging to eThekwini Electricity. The set-up consists of two 100 kVA transformers, one containing corrosive oil and the other containing clean oil. While varying the load and temperature of the transformer, oil samples were taken at various intervals and tested for corrosive sulphur by monitoring the concentration of dibenzyl disulphide (DBDS) and the dielectric strength of the oil. This data was used to investigate the reaction rates, activation energies and various thermodynamic parameters of the corrosive sulphur and Cu_2S, and to establish the factors affecting their formation.

At high temperatures, the DBDS concentration was found to reach equilibrium. The activation energy for the DBDS reacting with copper and further formation of DBDS was found to be 47.4 $KJmol^{-1}$ and 35.2 $KJmol^{-1}$ respectively. This research also determined that a significant amount of the initial concentration of DBDS was needed in order to react with copper. This experimental study also showed that DBDS and Cu_2S reactions do not play a major part in influencing the physical properties of the transformer and transformer oil. Surface physics concepts were employed to discuss the interaction dynamics of Cu_2S on copper surfaces. The main focus of the surface physics investigation compared the results from this experiment with results from other surface physics investigations in published literature.

Preface

The work described in this dissertation was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, Durban, from February 2011 to June 2013, under the supervision of Dr Mervlyn Moodley.

The studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

Declaration 1 – Plagiarism

I, **Sharlene-Asia Naicker** declare that

1. The research reported in this dissertation, except where otherwise indicated, is my original research.
2. This dissertation has not been submitted for any degree or examination at any other university.
3. This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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    a. Their words have been rewritten but the general information attributed to them has been referenced.

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I am very grateful to Yasheve Nageshar (Pr.Eng), Shane Piaray and Lenny Govender, from eThekwini Electricity Department, and Areno Singh from Eskom, who helped in the installation and running of the experiment as well as providing me with documents that were required to understand the installation. Their support, help and patience throughout this experimental project is greatly appreciated and acknowledged.

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Finally, my deepest and most sincere thanks and appreciation goes to my parents and my sister for their continuous support, love and the encouragement to follow my dreams. Their strength and prayer through difficult times provided me with added motivation that I will always appreciate and forever be grateful.

Om Namo Nataraja
Om Nama Shivaya
Om Marriamma

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Chapter 1

Introduction

Power transformers play a significant role in industry by converting high voltage to low voltage and vice versa [1]. In recent years, unexpected failures of power transformers have been observed worldwide. The transformer oil and the transformers had lacked prior warning of failure and passed international standards with regard to oil testing, before failing. The number of failures started to increase during 2003 and the reason for the failure at that time was unknown and not due to the overloading of the transformer [2].

Detail analysis of failed transformers indicated that transformer failures were caused due to the presence of corrosive sulphur in the transformer oil. Upon further investigation, the copper conductors and other copper surfaces were covered in films of copper sulphide [3]. As early as 1962, F.M Clark in the book titled, ”Insulating materials for design and engineering practice”, stated: ”Sulphur compounds are present in all commercial insulating oils” [4]. The different species of sulphur compounds includes mercaptans, elemental sulphur, sulphides, dibenzyl disulphide and thiophenes [5]. Sulphur compounds contained in transformer oil are not all harmful since sulphur is required for the oxidation stability of the transformer oil [6].

The common category of equipment affected by corrosive sulphur is oil-filled equipment which operate at relatively high temperatures [6, 7]. Corrosive sulphur is a major problem because it does not require heat to interact with copper. The influence of copper sulphide and corrosive sulphur also affects all companies that use oil based equipment.

The main mechanism leading to transformer failures involves the formation of conducting copper sulphide, whose chemical formula is given by Cu_2S [6]. This conducting compound increases the

thermal instability and decreases the dielectric breakdown of the insulating system.

Testing procedures were conducted to understand the corrosive sulphur phenomena. The majority of the testing procedures that are performed on transformers were developed by the ASTM (American Society for the Testing of Materials). These testing procedures allow any contaminants such as corrosive sulphur to be detected in the transformer. Testing also aids in identifying the influence of contaminants on the electrical, chemical and dielectric properties of transformer oil. Chemical testing is the most efficient method to test the transformer oil without opening the transformer. The different test methods conducted in this research will be explained further in the dissertation.

The surface physics concepts mentioned in this dissertation will provide a theoretical understanding of the interaction of atoms, such as Cu_2S on metal surfaces such as copper (Cu) conductors. Kinetic analysis is a key part in understanding any reactions that take place as well as understanding the influence of reactions. Kinetic analysis provides information about rate constants, activation energy and the pre-exponential factors.

1.1 Aims and Objectives

The aim of this study was to understand the role of corrosive sulphur and the formation of copper sulphide in transformers. The objectives of this study was the following:

- Identifying corrosive sulphur as a problem and determining the factors that accelerate the formation of both corrosive sulphur and Cu_2S .
- Determining the formation mechanism of the copper sulphide reaction.
- To use running transformers and oil tests to track corrosive sulphur and copper sulphide.
- To identify the kinetic parameters of corrosive sulphur and copper sulphide reactions and observe the influence of corrosive sulphur on transformer oil properties.

1.2 Thesis Overview and how to read this thesis

In Chapter 2, various concepts, definitions and case studies related to transformers are discussed. These concepts and definitions will be used throughout the dissertation.

In the third chapter, the different properties of corrosive sulphur and copper sulphide formation is discussed. This chapter also discusses the testing procedures that have been developed and the effect of copper sulphide on transformers.

Chapter 4 discusses the theoretical concepts that need to be considered in this dissertation. These sections include the kinetics of simple reactions and surface physics concepts which provide us with the background for the data analysis.

In Chapter 5, the insulation system is discussed since it is a significant part of the transformer that is affected by the corrosive sulphur. It describes the insulation system and the breakdown of the insulation system. The understanding of the insulation system provides an added motivation to investigate the copper sulphide and corrosive sulphur problem.

The last two chapters details the experimental setup used to study the corrosive sulphur situation and give a discussion of the results that were obtained from chemical tests performed on two transformers. These chapters discuss the necessary findings obtained from experimentally determining the influence of corrosive sulphur and copper sulphide on the transformer oil and the transformer.

Chapter 2

Introduction to transformers and its subsequent failures

2.1 Introduction

This chapter gives a brief description of transformers. All terminologies and definitions relating to electrical transformers used throughout this thesis can be found here. This chapter also includes details of the construction and operation of the transformers and possible causes resulting in their failures. For a more complete and technical discussion see [8, 9, 10] at the end of this thesis.

2.2 Transformers

The International Electrotechnical Commission (IEC) standard definition of a power transformer is :

"A transformer is defined as a static piece of apparatus with two or more windings which, by electromagnetic induction, transforms a system of alternating voltage and current into another system of voltage and current usually of different values and at the same frequency for the purpose of transmitting electrical power" [11].

A transformer consists of two coils namely the primary and secondary coils that are interwoven and linked by the core which is covered to reduce the eddy currents losses. Transformers are designed in such a way as to produce a magnetic flux and flux lines in the primary coil which in turn induces a current in the secondary coil. A voltage is applied to the primary coil and a magnetic

field is induced which will produce an ac voltage of the exact frequency in the secondary coil. This voltage will be different since it depends on the number of windings in the secondary coil [12]. Transformers are capable of being both step up and step down generators of power. The step up transformers are used to generate energy at a level suitable for transmission and occur since the secondary coils have more windings that the primary coils. In the step down transformer, secondary coils have twice as many windings as the primary coil [8, 12].

The power transmitted undergoes various transformations before reaching the final destination [12]. The path from generation of electricity, to the distribution of the electricity and finally the electricity being consumed is illustrated in Figure 2.1.

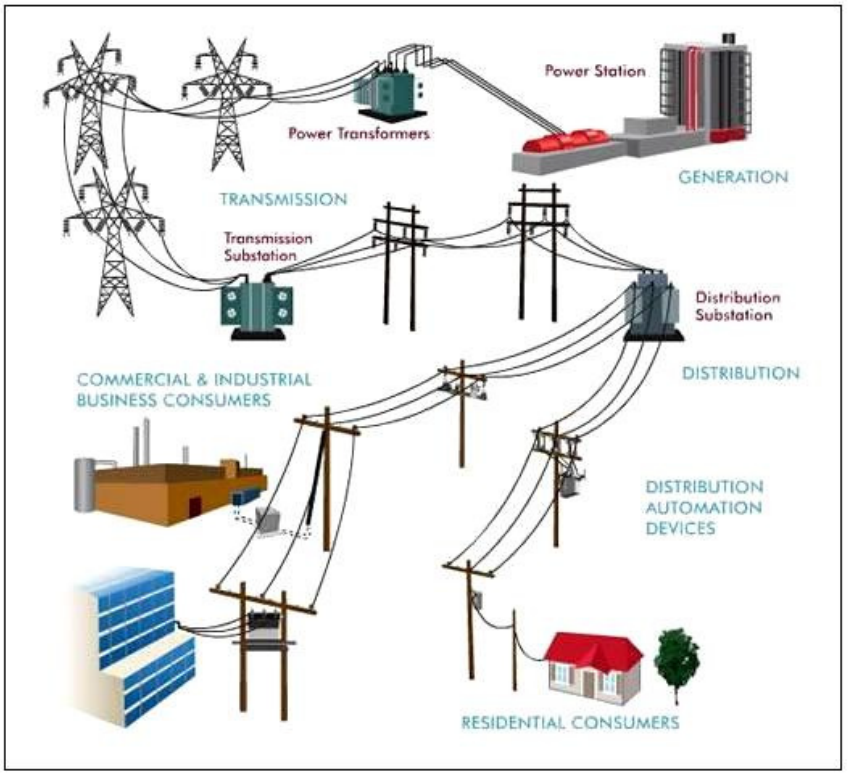

Figure 2.1: Electricity distribution of power transformers [13].

A cross-sectional view of a typical transformer is given in Figure 2.2. A transformer is highly efficient in drawing away the losses that occur in the core, windings and other parts. The magnetic core causes the alternating flux to create losses while the windings create direct losses and eddy currents. These losses heat the different areas of the transformer and oil is required to move the

heat away from the area and into a cooling medium [14]. Figure 2.2 illustrates the position of the core, windings and oil ducts with regard to each other.

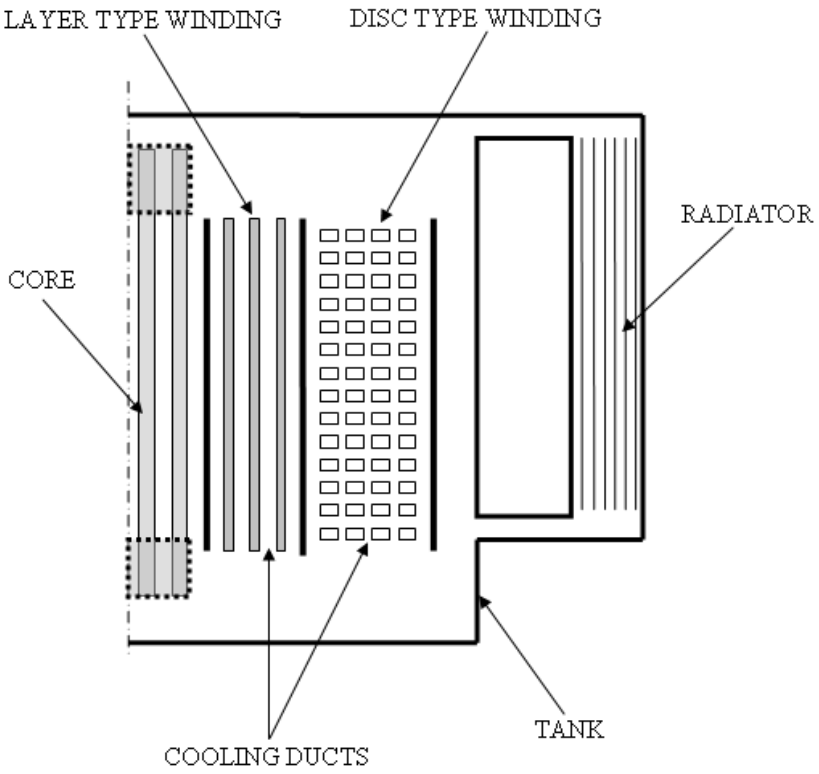

Figure 2.2: The cross sectional view of a transformer [14].

The transformers used in our experiment as described will be distribution transformers. The main functions of these transformers are to decrease the primary voltage of the system in order to provide the necessary power service [10, 15] .

Other types of distribution transformers, illustrated in Figure 2.3 and 2.4, includes pole-type, pad mounted, vault or network type and submersible type transformers. The distribution transformer is constructed with a lightning arrester, expulsion type fuse (which is normally stored under the oil tank), a secondary circuit breaker and warning light. The bushing conductor is connected to the one to three phase circuit [10, 15].

The transformer tank is grounded and connected to the primary and secondary ground wire which makes the distribution transformer fully grounded. Distribution transformers contain all the normal components which include coils, core, the primary bushing which holds a primary fuse, a reduced voltage circuit breaker and a secondary terminal block. The main feature that differentiates the typical transformer from this type of transformer is that the typical model does not include internal fusing [10, 15].

Figure 2.3: The pole type and substation distribution transformers [16].

2.3 Transformer Construction

Transformers are divided into four significant components: core, primary and secondary windings and insulation. The core and windings are where the functions of the transformer are performed. The insulation system of a transformer is sensitive as it is most effected by stresses and chemical reactions. The insulation system deteriorates rapidly and is significant since it determines the lifetime of the transformer [8].

Figure 2.4: Small and Large distribution transformers [16].

2.3.1 The Core

The two types of core constructions are core and shell-type. The core is made up of rolled up thin sheets of silicone steel laminations that are insulated from one another [8].

Core-type

The core-type consists of windings that are wrapped around the core as illustrated in Figure 2.5. The magnetic flux travels through the center of the core. Core-type constructions are advantageous since it uses less space and can be used for single to three phases systems.

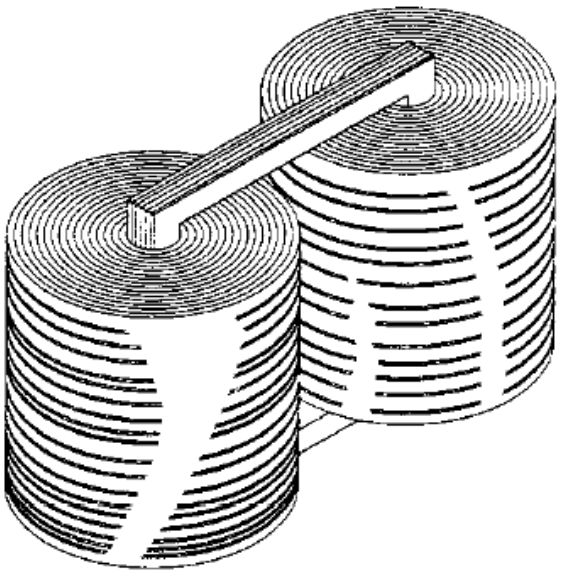

Figure 2.5: Core type construction [8].

Shell-type

The shell-type consists of windings wrapped inside the core as illustrated in Figure 2.6. This type of construction is used for larger transformers. The advantage of using such a system is for the variety of choice in winding construction. The magnetic flux can travel through both the core and around the windings [8].

2.3.2 Windings

The most significant operation of the transformer occurs in the windings. The primary windings provide a means for transporting the alternating current that creates the flux which eventually magnetizes the core of the transformer. The secondary windings are another set of means to transport the alternating current that was induced by the magnetized flux that radiates from the core of the transformer. The ratio of the number of turns in the primary to that of the secondary coils, given in equation 2.1 and 2.2 , determines the voltage and current output of the transformer [8].

The basic equation for the ratio of voltage is given by:

$$\frac{N_p}{N_s} = \frac{V_p}{V_s}, \tag{2.1}$$

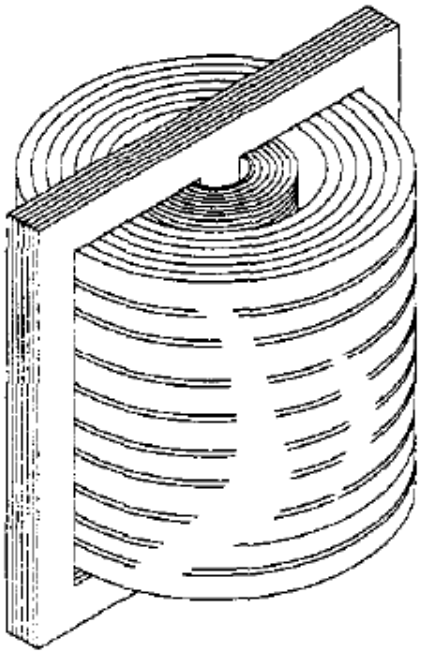

Figure 2.6: Shell type construction [8].

where N_p is the number of turns in the primary coil and N_s is the number of turns in the secondary coil. V_p is the voltage generated in the primary coil and the V_s is the voltage generated in the secondary coil.

The basic equation for the ratio of current is given by:

$$\frac{N_p}{N_s} = \frac{I_p}{I_s}, \tag{2.2}$$

where I_p is the voltage current in the primary coil and the I_s is the current generated in the secondary coil.

Transformer windings are made of two different material types namely copper and aluminium [17]. However, in the present day, copper seems to be the most popular choice for designing windings [17]. The biggest advantage of using copper windings is their greater ability to provide mechanical strength and a higher electrical conductivity. The windings can come in three different configurations: round wire, rectangular conductor or sheets. They are normally designed depending on the amount of current that they will be transporting. Round wire are used for high voltage distribution units since low currents are transported. The wire and rectangular conductors, however, prevent

the flow of charges less than the sheet conductors [17]. The windings are wrapped in insulation paper and arranged alongside the core [18]. The windings are designed to dissipate heat produced by eddy currents formed by the coils. Paper and wood spacers are normally added between these conductors which create space for cooler fluid to replace the heated fluid and thereby cool the system [17]. The windings are also able to withstand electrical stresses and mechanical stresses [18]. These electrical and mechanical stresses are as a result of the electrical and mechanical factors mentioned in section 2.5.1 and 2.5.2.

An alternating current is passed through the primary windings which creates a magnetic field with varying flux lines. The magnetic field lines can extend towards the secondary windings as indicated in Figure 2.7. A current is created by the flux moving across the conductor. The current in the primary winding then increases and the flux lines then extend further across the secondary windings which induces a potential difference on this winding. The energy transfer occurring between these two windings forms the basis of the transformer function. The magnetic flux increase further as the primary winding current is increased. The core is therefore used to direct these flux lines into the secondary windings. If the core material is iron then the flux moves more efficiently from the primary to the secondary windings which transfers energy as efficiently. The transfer of flux is illustrated in Figure 2.8.

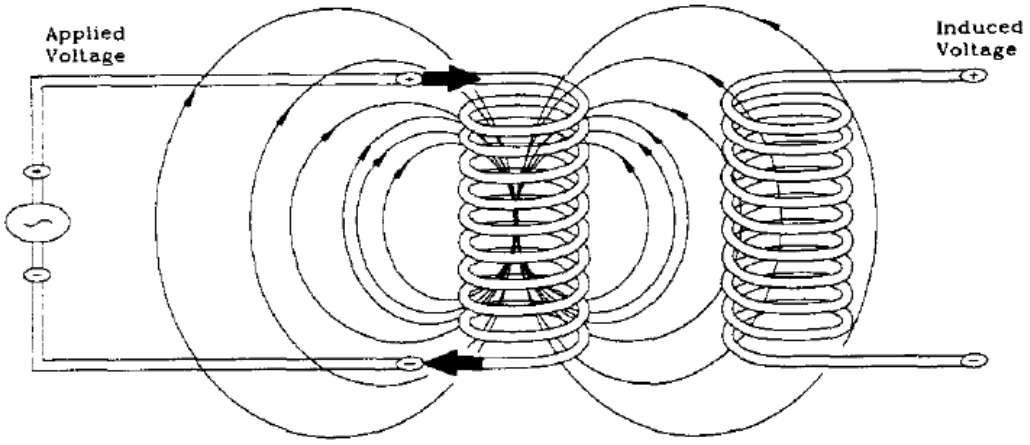

Figure 2.7: Current in the primary windings inducing a magnetic flux in the secondary windings [8].

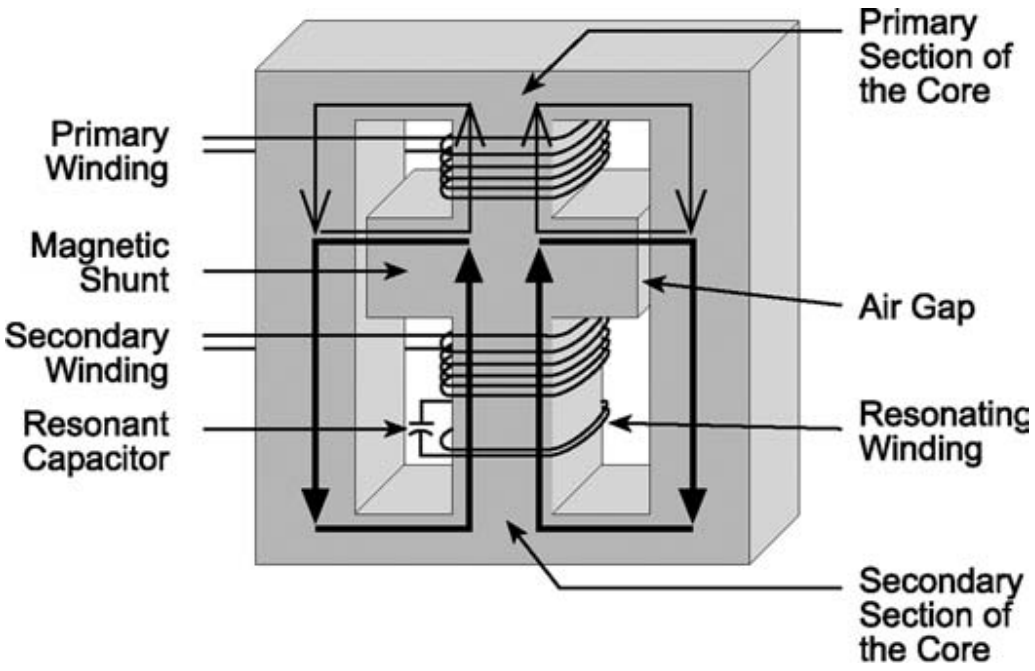

Figure 2.8: The primary and secondary windings along the core of the transformer [19].

2.3.3 Insulation

Liquid-Oil

The very first transformers did not contain transformer oil but rather used air as a dielectric and insulating medium. However, air was found to be insufficient in transporting heat away from the core or coils, whose heat was generated from the large energy losses in the transformers. The use of mineral insulating oil was then established and is now used as an effective dielectric medium in transformers [1].

The four functions of the transformer oil are as follows: to provide dielectric strength, to act as a cooling medium, to act as a separation medium between the paper and contaminants and to act as a tool to determine the state of the solid insulation. The development of contaminants due to aging and sludge affects the oil's ability to act as a coolant and also affects the insulation system of the transformer [1].

Solid-Insulation Kraft paper

The solid insulation is normally a cellulose-type compound such as Kraft paper. It is highly dependent on temperature, oxygen and acids and therefore degrades over time according to these factors. Heat and moisture have been identified as the most significant adversary against solid insulation. The life of a transformer can decrease by 40 to 60 years when the temperature is increased [20]. The breakdown of the solid insulation cause the cellulose glucose molecules to degrade and become shorter, resulting in compounds such as furan type molecules (furfural derivatives) and gases to be created and dissolved in the oil [20].

2.3.4 Cooling system

The cooling system of the transformer is composed of fans, pumps and water cooled heat exchangers that transfer heat from the core and windings [21]. There are various types of cooling systems. The different cooling systems together with its acronyms are given in Table 2.1.

Table 2.1: The different cooling systems and their abbreviations.

Acronym	Full Definition
OA	Oil Air Cooling
AN	Air Natural
ON	Oil Natural
OAFA	Oil Air Forced Air
ONAN	Oil Natural and Air Natural
ONAF	Oil Natural and Air Forced
OFAN	Oil forced and Air Natural
OFAF	Oil forced and Air Forced
OAFFA	Oil Air, Future Forced Air

Liquid filled transformers

Liquid-filled transformers have a similar cooling system to the dry-type transformers which are self-cooled and forced-air cooling system.

A self-cooled transformer depends on the surface area which can be increased by corrugating the tank wall or adding fins or radiators which extract the excess heat from the transformer system.

The varying heat inside the transformer creates convection currents inside the fluid which draws away heat from the core. The cooling class of these transformers is OA.

Forced air-cooling deals with introducing fans to the transformer system. Fans are used to circulate the air around the coils and can be manually or automatically controlled. The cooling class for forced-air cooling in oil-filled transformers is FA.

Pumps are another method to increase circulation of the oil in the transformer and thus increase the cooling capacity. The pumps increase the convection currents which transfers heat more rapidly through the transformer. The pump is also used together with the fans and is normally installed between the radiators and tank walls. The cooling class designation is OAFA [8].

Dry-type transformers can operate at temperatures of 150°C. Due to the slow response of air withdrawing the heat, the temperature is usually kept at 100°C. The use of air as a cooling mechanism and due to the high operating temperatures, transformers require adequate ventilation. Self-cooling or forced-air cooling systems is normally applied in dry-type transformers as a mechanism for cooling. The cooling class of this type of cooling is referred to as OA [8].

2.3.5 Tank Classification

An ideal transformer is a static device with no moving parts; the oil and tank are continuously expanding and contracting depending on the changes on temperature by voltage and current. As the oil increases in temperature, the transformer oil expands and air is absorbed into the transformer as mentioned in Chapter 6.

It has been observed that thermal expansion causes the oil level to increase or decrease by as much as 500ml. This change in oil level occurs when the air that is absorbed into the transformer contaminates the transformer oil. Tanks are being constructed to deal with the expanding of the oil and to prevent further contamination of the oil. The following is a brief description of various types of tanks [8].

Free Breathing Tanks

Free breathing tanks operate at atmospheric pressure. These tanks are at a greater risk of sludging since they are continuously in contact with air. Methods to remove the moisture are implemented to prevent the oil from being contaminated. Dehydrating compounds in the tank need to be maintained regularly since irregular maintenance will cause excess moisture and sludging to develop [8].

Conservator Tanks

These tanks use a separate tank to prevent the oil and air from interacting. The main tank consists entirely of oil. The small conservator tank is attached to the top of the main tank. The main tank will not contain sludge since the conservator tank absorbs all the water and sludge. Gases can form in the conservator tank and therefore it is necessary to remove gases periodically from the tanks.

Gas-oil Sealed Tanks

The gas-oil sealed tank is the same as the conservator tank such that the auxiliary tank's oil is separate from the main tank oil. The oil levels of both the tanks can therefore change but the oil never comes in contact with each other or the atmosphere. The oil is drained often to prevent further contamination and failure.

Automatic inert gas sealed tanks

Some transformers use inert gases to prevent contamination of the transformer system. These are rather costly and difficult to maintain, however, highly effective at preventing contamination.

Sealed tank types

These are the most popular construction type. The tank is sealed and consists of strong walls which are designed to allow a small amount of contraction and expanding. A nitrogen gas blanket is placed over the main tank which helps absorb the pressure fluctuations. A slight pressure existing in the transformer prevents any influx of air and liquid.

2.4 Classification of the different types of transformers

Transformers are classified into two main categories namely the core and shell-type transformers. However, the standard classification of transformers depends on their construction and specifically on how the heat in the transformer is dissipated. Classification of transformers can also be made according to tank construction. The two unique types of transformers include liquid-filled transformers and dry-type transformers [1, 8].

2.4.1 Liquid-filled Transformer

Liquid-filled transformers are the most popular of the transformer types and are used in the majority of power supply industries because of their ability to handle large amounts of power output. Liquid-filled transformers have an advantage because they can transfer heat faster through the transformer. The liquid transfers heat from the main tank, the core and the windings. The liquid also acts as an insulator, however, oils and other fluids lose their ability to insulate at high temperatures and therefore liquid-filled transformers operate at low temperatures at about 55 °C.

2.4.2 Dry-Type Transformers

Dry-type transformers use air circulation to draw away heat that is formed by the transformer's losses. The advantage of using dry-type transformers is that no oil corrosion can take place since there is no oil in the transformer. These transformers also depend on the surface area to remove heat from the system. Dry-type transformers also require less maintenance, however, dirt blankets that are sometimes formed, need to be cleaned out.

There exists many challenges to using dry-type transformers. These transformers also operate at higher temperatures but are not able to lose heat fast enough as compared to using oil filled transformers. Since these transformers use air as a method of cooling, the losses are higher as compared to liquid-filled transformers. Dry-type transformers fail faster than liquid filled transformers and therefore require more insulation in the windings [1, 8].

2.5 Typical Failures

This section will discuss the typical failures that take place in transformers. It will identify the main factors that contribute towards failures of transformers. Failures are said to occur when the

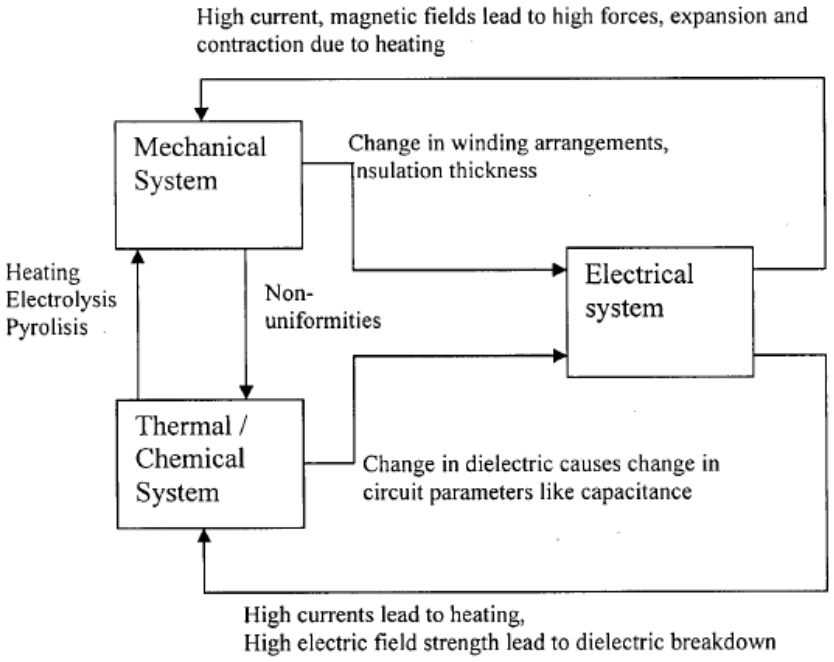

Figure 2.9: The different systems in a transformer [22].

insulation system of the transformer breaks down.

The workings of a transformer are divided into three different systems. These are, the electrical system, the mechanical system and the thermal/ chemical system and are illustrated in Figure 2.9.

Below is a brief description of the electrical, thermal and mechanical factors that influence the failure of transformers [9].

2.5.1 Electrical influential factors

These factors cause the insulation system to fail and can occur simultaneously with the other failure modes. The electrical factors include allowing the transformer to operate over the normal voltage for a short period of time which causes partial discharge.

2.5.2 Thermal influential factors

The degradation of the insulation system is influenced greatly by the temperatures of the transformer. Thermal factors can also occur simultaneously with the other failure modes. Overheating is typically caused by the following: the overloading of the transformer; the failure of the transformer cooling system which results in a failure in the heat distribution system and the oil ducts being blocked which reduces cool oil from being transferred to the windings.

2.5.3 Mechanical influential factors

Mechanical faults causes destruction of the windings which results in a deformation of the insulation system. The destruction of the windings can happen during shipping or electromechanical problems and incorrect design features.

2.6 Identification of corrosive sulphur as another cause for failure

In this section we discuss various case studies that have led to the identification of copper sulphide as a cause for transformer failures.

Since 2000 a number of large transformers and reactors have failed. These units have been operating for approximately 5 to 7 years of age [23]. The failures had no warning from dissolved gas analysis (DGA) tests or other test methods that were implemented [24]. Four significant case studies were done to investigate the failure of transformers due to corrosive sulphur and copper sulphide.

The first case study by Simon Ryder [25] discussed a 1000 MVA transformer installed in 1994 in North East England that had failed suddenly in May of 2007. Dissolved gas analysis gave no warning of failure, however, there was a small amount of furans (degraded glucose molecules that is released when solid insulation breaks down [26]) in the oil which was unusual for this type of transformer. The damage was so severe that a precise location of initial position of failure could not be identified. The evidence of copper corrosion was found on the outer windings. After a thorough investigation it was discovered that the windings were designed using manufacturing standards which resulted in no oil being able to circulate through the oil duct in the winding discs. This therefore created the optimum conditions for the formation and growth of copper sulphide: high temperature and low oxygen. The extent of the damage in the windings is illustrated in Figure

2.10.

Figure 2.10: The damage to the inside of the c-phase section [25].

The second case study by Lance Lewand [27] discussed the failure of a large transformer that occurred in July 2004. Initial oil analysis indicated that the oil was in excellent condition. The dissolved gas analysis test was performed a day before the transformer failed and this did not give any warning of failure. Failure of the transformer took place after a hole was formed in the inner part of the winding disk as illustrated by Figure 2.11. It was observed that black and grayish deposits were found on the copper conductor and on the insulation paper. By using a scanning electron microscope (SEM) and energy dispersive x-ray (EDX) analysis, it confirmed that the blackish gray deposits were copper sulphide. This case study indicated that the copper corrosion is more likely to occur at the top and bottom set of the windings rather than in the middle set of windings. It was diagnosed that the failure occurred due to the formation of copper sulphide in the insulating paper on the windings which reduced the dielectric strength of the oil.

In 2006, the Salt River project (SRP) [28] did a case study on a number of failed transformers in Arizona after a significant number of failures had occurred in 2004. 230 transformer oil samples were taken to be tested for corrosive sulphur. 38 had failed a standard corrosive sulphur test while 3 had failed both the standard and modified corrosive sulphur test. The fact that three previously

Figure 2.11: The damage to the inside of the c-phase section [27] .

normal transformers began suddenly displaying evidence of corrosive sulphur in the oil was a reason for concern. This case study had aimed to identify corrosive sulphur as a problem.

The final case study by G.M Bastos et al. [29] discussed the evidence of 10 failed transformers occurring from 1997 to 2004. A detailed investigation revealed copper sulphide deposits on the conductor and paper insulation. It identified that high temperatures in certain parts of the transformer caused the oil to convert the stable sulphur compounds to reactive sulphur compounds as evident from copper sulphide deposits.

The above case studies tell us that there seems to be a correlation between the manufacturing design of the transformers and the formation of copper sulphide. The conditions of corrosive sulphur such as high temperature and a lack of oxygen seems to be evident in all of the case studies. The aging of solid insulation is also a major factor in the failure of the transformers. Manufactures should therefore be wary of the oil ducts and the position of the oil ducts in the transformer since the lack of oil flow results in the lack of cooling and the increase of the temperature in the transformer.

Chapter 3

Corrosive Sulphur

3.1 Characteristics of Corrosive Sulphur

3.1.1 Sulphur in transformer oil

Transformer oil consists of about 100 different sulphide compounds and a small amount of these sulphides are reactive or corrosive [30, 31, 32]. The total sulphur content in the transformer oil ranges from 0.01% to 0.5%. The more prominent forms include elemental sulphur, mercaptans, cyclic sulphides, thiophens, disulphides and polysulphides [33]. The oil used in transformers is processed from crude oil. Sulphur occurs naturally in crude oil which also contains other elements such as nitrogen and oxygen [34].

Some sulphur compounds have been found to benefit the oil by acting as retardants or passivators to the oil and preventing the oxidation process [35]. These sulphur compounds are called the oxidation inhibitors and are the non-corrosive sulphur component [17, 24, 31, 36]. Since natural inhibitors are present there would be no need for synthetic oxidation inhibitors. If we were to remove all the sulphur in the transformer, we would not have a resistance to the oxidation process. The oxidation process forms harmful contaminants such as acid which decreases the breakdown voltage of the insulation system of the transformer [32]. The sulphur responsible for inhibiting the oxidation process is the main corrosive sulphur that reacts with copper to form Cu_2S [36]. Excess sulphur can also be present in the components of the transformer such as gaskets and the glue that is used to put the transformer together. Sulphur can also be part of the bare copper windings composition [19].

The total sulphur content in the transformer was found to fluctuate from 1964 with an increase and decrease between 1964 and 1980 [34]. Thereafter, as illustrated in Figure 3.1, a downward decrease of sulphur content in the oil began in 1990 due to an improvement in the refining process [34]. The graphical plot, given in Figure 3.1, shows the decrease in sulphur content in transformer oil during the last 4 decades. Figure 3.1 shows that the concentration of sulphur was the highest between 1965 and 1980 with concentrations of 3000 mg/kg while the lowest concentrations occurred in 2000 and have held steady at about 250 mg/kg. The largest difference between the concentrations of sulphur is due to the lack of proper refining techniques. The refining process removes unwanted substances that are present in the crude oil [37]. However, the refining process is not always fully successful and leaves behind the reactive sulphur [23]. Due to the severity of transformer failures, efforts were made to reduce sulphur content by a more stringent testing policy [34].

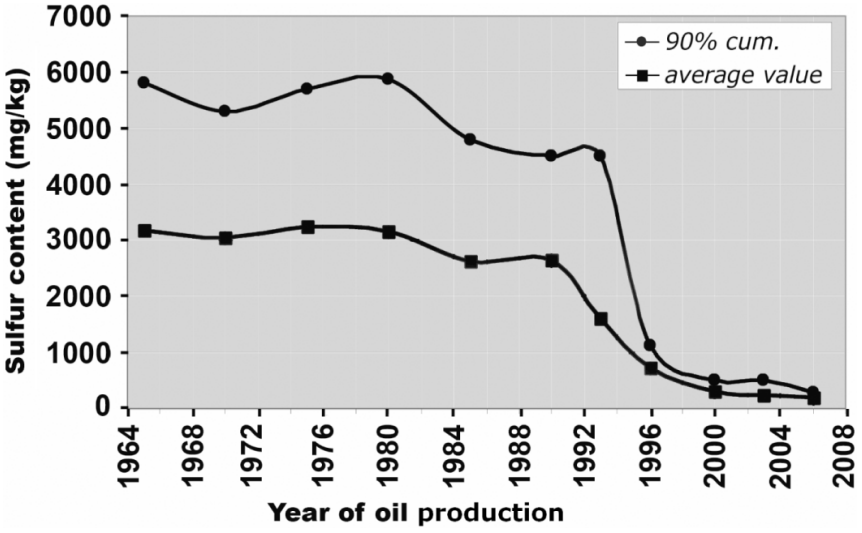

Figure 3.1: The decrease in sulphur content in transformer oil during the last four decades [34].

The corrosive sulphur problem has been investigated from the mid 1990's whereas the presence of sulphur in all insulating liquids was discovered from 1962 [38]. Sulphur compounds have been found to cause corrosion while increasing the formation of sludge and thus affecting the electrical properties of the transformer oil. Some studies have found that corrosive sulphur is not always formed during the operation of the transformer but formed during the refining process [34].

3.1.2 Corrosive sulphur in transformer oil

The definition of corrosive sulphur in transformer oil as stated by the ASTM[1] D 2864 test , is :

"Elemental sulphur and thermally unstable sulphur compounds in electrical insulating oil that can cause corrosion of certain transformer metals such as copper and silver" [39].

The simple accepted definition of corrosive sulphur is, sulphur that has turned corrosive and affects the components of the transformer at normal operating temperature [35]. Certain types of corrosive sulphur have been identified to exist in the transformers that have failed. These are the disulphides and the mercaptans which are compounds of sulphur. The dibenzyl disulphides were found to exist in large amounts while the mercaptans were found to exist in small amounts. Dibenzyl disulphide is the most common sulphur compound to cause corrosion [35, 40]. The degree of corrosion of the oil is dependent on the type of corrosive sulphur, the amount of copper available in the system and the type of mineral dielectric insulating oil. It is also dependent on the temperature and the amount of time the copper conductor was exposed to heat. Gas chromatography and atomic emission tests are used to analyse samples that are suspected to contain corrosive sulphur [35]. The gas chromatography result given in Figure 3.2 identifies that the sulphur responsible for corrosion in both old and new transformers is dibenzyl disulphide (DBDS). This is illustrated by the dibenzyl disulphide producing the largest peak for the total sulphur compounds in the sample [41].

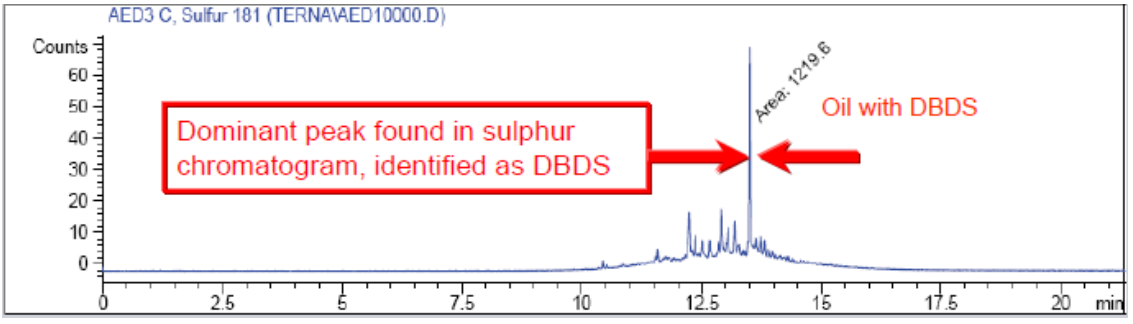

Figure 3.2: The typical evidence of DBDS in the chromatograph [41].

[1] American Society for the Testing of Materials (ASTM)

3.1.3 Dibenzyl disulphide

So far there has been no specific corrosive sulphur that was found to cause the problem of copper sulphide formation. Most researchers agree that the cause could be attributed to the presence of mercaptans, a sulphide compound with a different functional group, while others have focused on the corrosive sulphur known as dibenzyl disulphide [40], to be the main instigator in the formation of copper sulphide in transformers [38].

DBDS is a highly reactive species which was initially considered highly stable and a least reactive compound. However, recently it was found that DBDS is more susceptible to breaking down into highly reactive sulphur namely mercaptans [30, 36]. The DBDS molecule itself can be either corrosive or non-corrosive and it is also used in oil to decrease friction [40]. The amount of DBDS in the oil can vary from 100 to 1000mg/kg [30, 36, 40].

It has also been found that corrosive sulphur reacts at temperatures of 80°C with the copper conductors [30, 36]. The most stable type of sulphur compound in the oil is thiophenes. However, it has been found that under thermal stress and enough time, the thiophenes also break down and become highly reactive [30, 36]. Research in corrosive sulphur identified DBDS as being the main sulphur found in a majority of failed transformers [30, 38, 40, 42, 43].

The reasons that this research focuses on DBDS is:
1. The breakdown products of the DBDS have proven to be harmful which causes further corrosion in transformer oil.
2. The transformers that have failed had a higher presence of DBDS in the oil.

The chemical structure of DBDS is shown in Figure 3.3. The chemical formula is $C_{14}H_{14}S_2$ and its molar mass is 246.60g [40].

The formation of DBDS-copper (Cu) complex is said to play an integral part in reacting with the copper that migrates from the copper windings and then forming copper sulphide on the copper surface [40]. The DBDS-Cu complex is the first reaction in a series of reactions that eventually form copper sulphide which deposit on copper surfaces [30, 36].

The degradation of DBDS and the formation of copper sulphide as illustrated in Figure 3.4 reveals

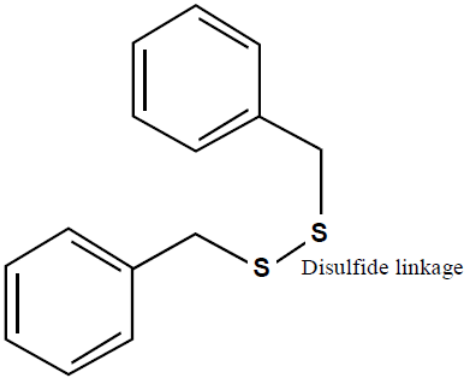

Figure 3.3: The theoretical structure of DBDS [40].

that DBDS degrades first into benzyl mercaptan. Degradation occurs when DBDS is exposed to high temperatures which breaks down its chemical bonds. These breakdown by-products causes further damage [40] since they are corrosive. The copper sulphide is thereafter formed when benzyl mercaptan oxidizes. A small amount of H_2O is also formed during the reaction however the concentration is almost negligible [30, 36].

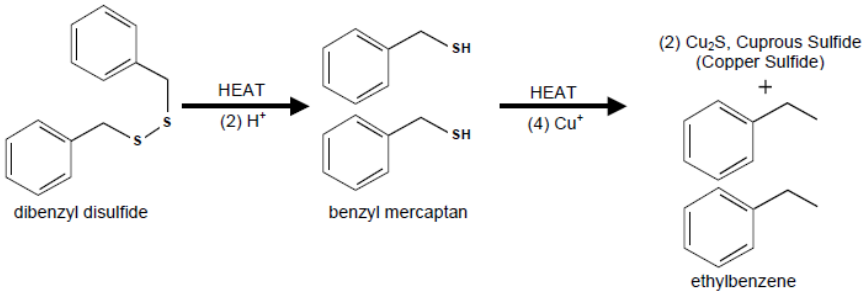

Figure 3.4: The degradation of DBDS [40].

3.1.4 Copper sulphide in general

The general chemical formula for copper sulphide is Cu_xS_y. The copper sulphide dealt with in this dissertation is the Cu_2S [32]. Copper sulphide consists of three different isomers. The first isomer is chacolite which is the elemental sulphide that is found in the earths crust [44]. The second isomer is copper monosulphide (CuS) which has one less copper ion than Cu_2S and the final sulphide isomer is cuprous sulphide which is the general copper sulphide (Cu_2S) [32, 44]. The colour of

copper sulphide corrosion ranges from being bluish grey to black and then to green which makes the identification of the deposition of copper sulphide to be difficult [32]. Cu_2S is also insoluble in water. The basic interaction of copper (Cu) and sulphur (S) is given by [44]:

$$2Cu^{+1} + S^{-2} = Cu_2S \tag{3.1}$$

Copper sulphide has a molar mass of 159.16 g/mol, density of 5.6 g/cm^3 and a melting point of 1130°C [44].

3.1.5 Formation Mechanism

This section discusses the different formation mechanisms of copper sulphide in the copper windings and in the transformer oil [43].

The first mechanism of the formation of copper sulphide involves the copper ions traveling from the copper conductor into the oil and leaving vacant sites in the copper conductor. Figure 3.5 illustrates the vacant sites formed in the copper conductor when copper migrates into the oil. The corrosive sulphur, dibenzyl disulphide which is present in the oil, reacts with the copper ions in the oil and forms partially conducting copper sulphide. The copper sulphide then deposits on the copper conductor and in the vacant sites of the copper conductor .

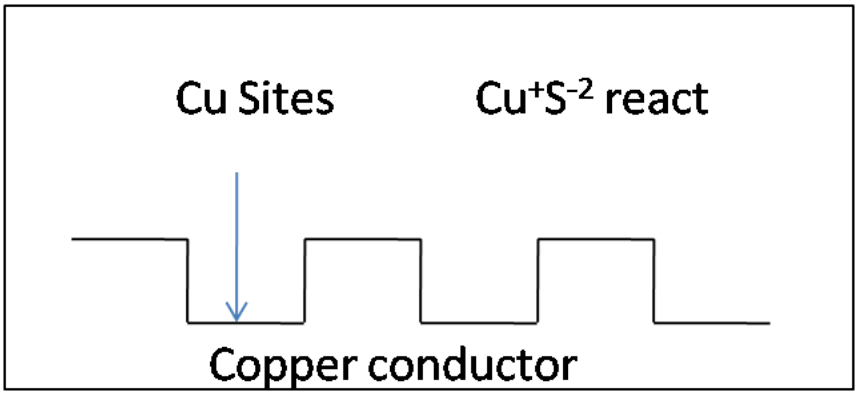

Figure 3.5: The copper conductor with copper sites created when the copper ions migrate into the transformer oil.

The second mechanism involves the copper sulphide being formed when the copper surface (copper winding) interacts with the corrosive sulphur (dibenzyl disulphide) in the oil. The copper sulphide forms on the copper surface and embeds itself into the copper conductor. Figure 3.6 shows the buildup of copper sulphide in and on the copper conductor .

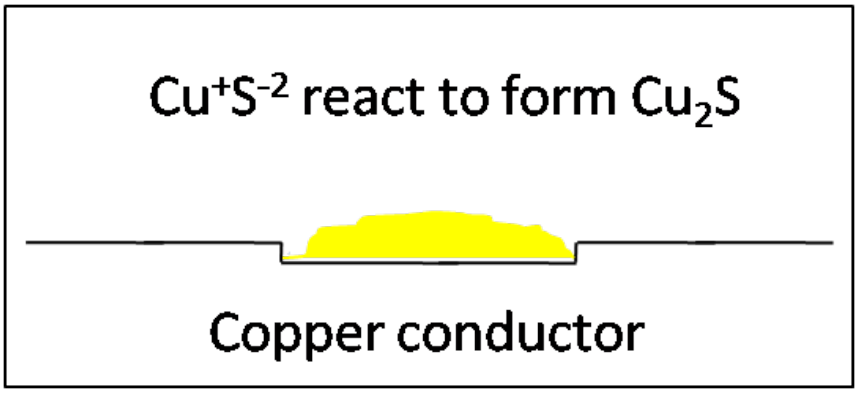

Figure 3.6: The buildup of Cu_2S that causes a distortion on the copper conductor.

The step by step formation mechanism of copper sulphide is illustrated in Figure 3.7. The first step is the interaction between DBDS and copper to form the DBDS-Cu complex as mentioned in section 3.1.3. The second step is the degradation of the DBDS-Cu complex which forms copper sulphide. This copper sulphide then deposits on the copper surface.

The formation of copper sulphide from the copper reacting with the corrosive sulphur and other by-products is described by the following chemical equation [43]:

$$\text{Copper} + \text{DBDS} \longrightarrow \text{Copper sulphide} + \text{By-products}$$

$$4Cu + (C_6H_5CH_2)_2S_2 \rightarrow 2Cu_2S + C_6H_5CH_2CH_2C_6H_5$$

The conductive copper sulphide deposited on the copper surface causes a voltage change to occur on the windings in the transformer due to the increase in resistance. A voltage increase results in an overload in the transformer which results in it ultimately failing. The voltage change can also cause a distortion/deformation in the copper windings if the voltage is the same as the breakdown voltage of the copper windings. The distortion creates a breakage point in the windings [3].

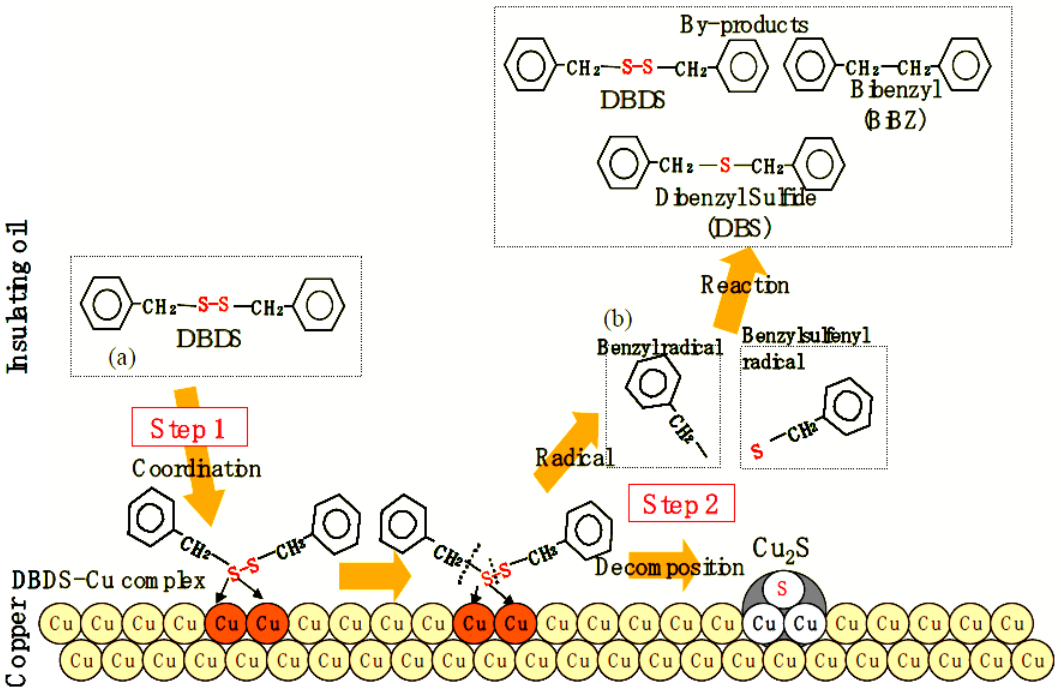

Figure 3.7: The formation of copper sulphide from DBDS [43].

The chemical process of corrosion also leads to the blackening of copper and the silver components in the transformer as illustrated in Figures 3.8 and 3.9. The corrosion in Figure 3.9 is circled in red. The most severe factor was identified as being the actual distortion and deformation of the copper conductors due to copper sulphide deposits [6]. The deformation of the copper conductors affects the solid insulation. Some investigations have found that the formation actually occurred in the inner areas of the cellulose paper [3, 6, 40]. Further investigations have shown that the deposition occurs on the conductor itself [6].

3.1.6 Corrosive Sulphur Historic Timeline

Table 3.1 and 3.2 respectively provide a tabular view of the progress made over the years with regard to corrosive sulphur detection and the different test procedures that have been developed. As indicated in Table 3.1, the problem of corrosive sulphur and copper sulphide formation was studied from as early as 1953 and currently is still under investigation. Some of these tests shown in Table 3.2 are the standard testing procedures used in transformer maintenance [38].

Figure 3.8: The paper wrapped conductors that have evidence of copper sulphide [38].

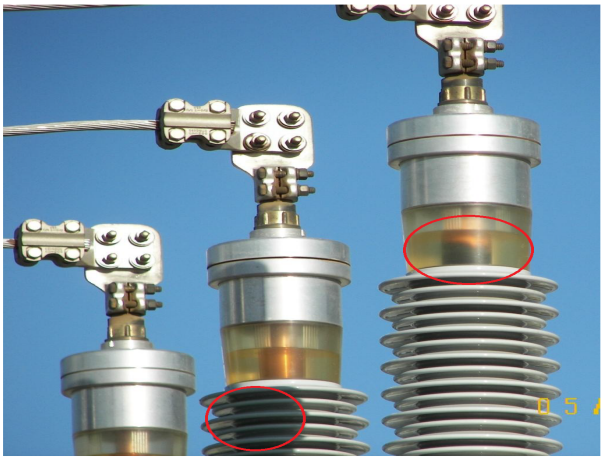

Figure 3.9: The copper and silver contacts that are affected by the corrosive sulphur [38].

More than a 100 large power transformers failed in 2004 worldwide [5]. The failures occurred in areas of warmer climate such as Brazil. The development of copper sulphide is not related to the age of the transformer. Old and new transformers have both displayed copper corrosion [38].

Table 3.1: The evolution of testing procedures for corrosive sulphur from 1953 to 2007 [38].

Date	Description
1953	FM Clark made the ASTM D 1275 test to detect corrosive sulphur.
1978	ISO 5666 test similar to ASTM D 1275 was created.
1985	DIN 51 353, corrosive sulphur test, developed by the Germans.
2003	Doble Engineering modified the ASTM 1275B test .
2004	Doble Engineering also created a new method for passivation.
2006	The ASTM committee accepted the Doble modified test.
2005	ABB created a Covered Conductor Deposition(CCD) test.
2006	Doble and Siemens created a CCD test
2006	Cigre developed a test method similar to the ASTM D 1275B.
2006/2007	The Covered Conductor tests were approved by the IEC.
2007	Doble Engineering created a test for DBDS.

3.2 Factors influencing the copper sulphide formation

Identifying the factors that play a role in the formation of conducting copper sulphide would bring us closer to the understanding of corrosive sulphur and mitigation procedures can thereafter be implemented to reduce the development of copper sulphide and corrosive sulphur.

Transformer oil contains normal sulphur compounds that are formed during the refining process. However, due to thermal effects and the extended time spent in the transformer, the non-corrosive sulphur becomes corrosive and reduces the oxidation stability of the transformers which eventually leads to the failure of the transformer [17].

The factors that influence the failure of these ‘healthy’ transformers include the type of oil used in the transformer and the temperature of the transformer along with the design of the transformer [6, 7].

Table 3.2: Different testing procedures developed for corrosive sulphur detection in transformer oil [38].

Test	Description
ASTM D130	Corrosives Sulphur in Petroleum Oils Maintenance testing
DIN 51 535	Corrosive Sulphur using a Silver Strip.
ASTM D 1275A	Corrosive Sulphur in Insulating Oil using copper strip.
ISO 5662	Detection of Corrosive Sulphur.
ASTM D1275B	Corrosive Sulphur in Insulating Oil modified from the ASTM D1275A.
ASTM D 5623	Sulphur Speciation.
ASTM D 4294	Total Sulphur in Oil.
ASTM D 3227	Mercaptans in Oil.
UOP 286/387	Elemental Sulphur.
CCD Test	Doble Covered Conductor Test.
IEC 62535	Detection of Potentially Corrosive Sulphur.
CCD +RT	Doble Covered Conductor Test with Resistivity.
DBDS in oil	Presence of Dibenzyl Disulphide in the oil used by Doble Engineering .
Tappi 406/444	Reducible Sulphur in Paper and Tarnishing in paper and pressboard.

In what follows, the various factors that lead to the failure of transformers due to corrosive sulphur will be discussed.

a) Oil containing dibenzyl disulphide

As mentioned in previous sections, DBDS is added to oil as an additive to prevent oxidation and decrease friction. It was observed that oil containing the corrosive sulphur itself was a main factor in the formation of copper sulphide and further formation of corrosive sulphur. Depending on the specifications of the oil, different oil manufacturing companies introduce a specific amount of corrosive sulphur in their oils. This results in different oil brands containing varying amounts of corrosive sulphur which create different concentrations of copper sulphide as illustrated in Figure 3.10 . Figure 3.10 also shows that there is a direct relationship between the heating time of a sample and the deposition of copper sulphide on surfaces [45].

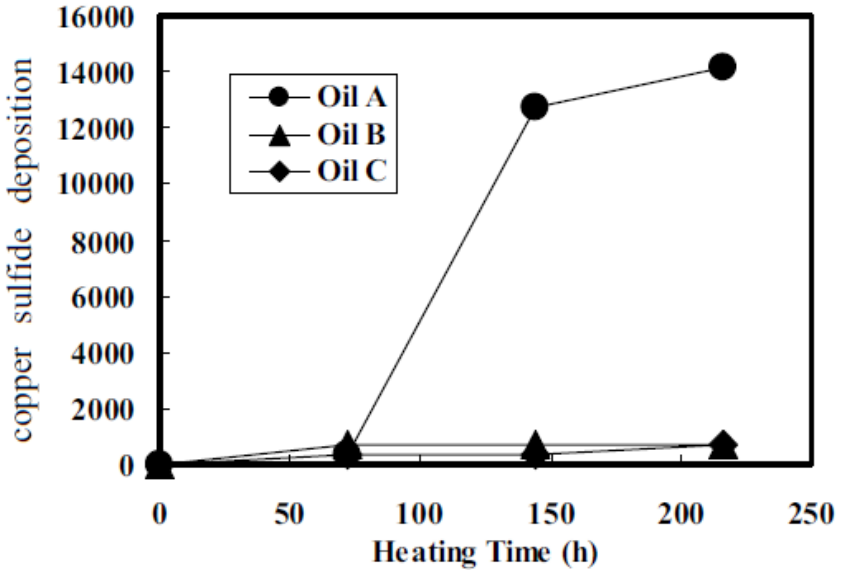

Figure 3.10: Different oils can have a different influence on deposition of copper sulphide (cps) adapted from Nagao et al. [45].

b) Concentration of copper dissolved

If the copper windings in the transformer are not coated with enamel, they are at a greater risk of interacting with the copper sulphide present in the oil. The lack of enamel also allows the copper ions to dissolve into the oil and react with the corrosive sulphur [6].

c) Temperature

The temperature of the transformer has a strong influence on the formation of corrosive sulphur. Chemical reactions increase when the temperature increases. However, the copper sulphide is not always formed in areas of high temperatures [6]. In some cases, the areas of copper sulphide deposition contain no evidence of elevated temperatures. It was found that corrosive sulphur form at temperatures between of 80°C and 150°C [6, 7]. Tests conducted as indicated in Figure 3.11 shows that temperature influences the deposition of copper sulphide. In the above study, thermal aging tests were performed on transformer oil samples at three different temperatures. The figure shows that the copper sulphide deposition was different at each applied temperature. As mentioned earlier in this chapter, high temperatures degrade the stable dibenzyl disulphide into reactive species which increases copper sulphide deposition [5].

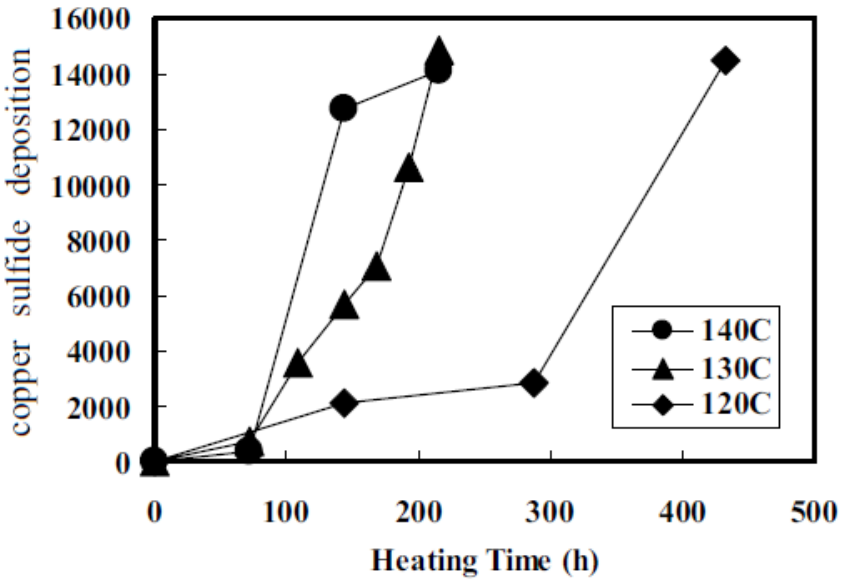

Figure 3.11: The different temperatures (120°C - 140°C) influence on copper sulphide deposition (cps) adapted from Nagao et al. [45].

b) Design of the transformer (cooling and lack of oxygen)

The quality of design of the transformer is also a factor leading to the failure of transformers. Both sealed and unsealed designed transformers have displayed evidence of copper sulphide formation in their oil [6]. Sealed transformer units have less oxygen molecules in the oil and therefore a poor oxidation stability so an increase in corrosive sulphur compounds is likely to occur. The unsealed transformers have more oxygen molecules than sealed units which causes the corrosive sulphur to become reactive [36, 46].

Another factor that contributes to copper sulphide formation is the poor design feature in the placement of the cooling system. The position and the number of cooling ducts influences the formation of copper sulphide. The wrong placement of cooling ducts increases temperatures and causes a lack of oxygen which would be optimum conditions of formation of copper sulphide.

The following chapter will discuss the theoretical aspects to consider when the understanding reactions and mechanisms of interactions.

Chapter 4

Theory of reaction and interaction mechanisms

4.1 Kinetic Theory

Kinetic theory of reaction mechanisms is a key factor in understanding the rate of formation of copper sulphide in transformer oil. In this chapter, the rate constant and the factors influencing the rate equation is discussed. The Arrhenius equation and thermodynamic parameters for reactants will also be discussed.

4.1.1 Rate of reactions

The time taken for a reaction to occur is called the rate of reaction or the reaction rate. The requirements for reactions to occur and the factors influencing the rate of reactions [47]:

- Molecules must interact/collide with one another.
- Molecules need to have enough energy to react with each other.
- The chemical equation of the reaction must be balanced such that the number of moles on left side of the equation is equal to the number of moles on the right side of the equation [47, 48].
- The orientation of the molecules must be well aligned so that the free valence bonds interact freely.

There are three factors that influence the rate of reactions [47, 48]:

- The chemical nature of the interacting molecules.
- The concentration of the molecules. An increase in the concentration of molecules results in more collisions occurring and a greater reaction rate.
- Temperature effects the frequency of collisions and therefore the rate of reactions.

A typical bimolecular reaction with two reactants, X and Y reacting to form the products Z is:

$$\mathrm{X} + \mathrm{Y} = \mathrm{Z}. \tag{4.1}$$

The definition of the rate of reaction is the time taken for the formation of products (Z) and the decrease of reactants (X + Y).

The rate of change in concentration of each molecule is given as [49]:

$$\text{Rate} = \frac{d[\mathrm{Z}]}{dt} = -\frac{d[\mathrm{X}]}{dt} = -\frac{d[\mathrm{Y}]}{dt}. \tag{4.2}$$

The overall rate equation for reaction 4.1 is represented as,

$$\text{Rate} = k[\mathrm{X}][\mathrm{Y}], \tag{4.3}$$

where k is the rate constant and [X] and [Y] are the concentrations of the reacting molecules. The rate constant (k) relates temperature to the rate equation, as will be seen in the section 4.1.3 [49].

Reactions can travel in both forward and reverse directions, however, in this dissertation, we focus only on forward reactions which are labeled as k_1 in equation 4.4 and given below:

$$\mathrm{X} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z, \tag{4.4}$$

where k_2 is the rate constant for the reverse reaction.
The forward reaction of equation 4.1, with a rate constant k, can also be written as [49]

$$\text{Rate} = k[\mathrm{X}]^m[\mathrm{Y}]^n, \tag{4.5}$$

where m and n is the order of the reaction.
The order (m and n) of the reaction influences the rate of the reactions and its dimensions (units) [49].

4.1.2 Order of reactions

Zero Order of reaction

In a zero order reaction, the rate of the reaction is equal to the rate constant (k):

$$\text{Rate} = k. \tag{4.6}$$

The units for the rate constant are mol.dm^{-3}.
The zero order rate equation is given by:

$$\frac{-d[\text{X}]}{dt} = k, \tag{4.7}$$

where [X] is the concentration of the X reactant [50].
If a plot of $[\text{X}]$ versus time produces a linear graph, it would indicate that the reaction is zero order.

First Order of reaction

In a first order reaction, the reaction rate is equal to the rate constant multiplied by the reactant as follows:

$$\text{Rate} = k[\text{reactant}]^1. \tag{4.8}$$

The units for the rate constant are $\frac{\text{mol.dm}^{-3}.\text{s}^{-1}}{\text{mol.dm}^{-3}} = \text{s}^{-1}$.

The first order rate equation is given by [50]:

$$\frac{-d[\text{X}]}{dt} = k[\text{X}]. \tag{4.9}$$

If a plot of ln[X] versus time produces a linear graph, it would indicate that the reaction is first order .

Second order of reaction

In a second order reaction, the reaction rate is equal to the rate constant multiplied by the reactant squared.

$$\text{Rate} = k[\text{reactant}]^2. \tag{4.10}$$

The units for this rate constant are $\frac{\text{mol.dm}^{-3}.\text{s}^{-1}}{\text{mol.dm}^{-6}} = \text{mol}^{-1}.\text{dm}^{-3}.\text{s}^{-1}$.

The second order rate equation is:

$$\frac{-d[\mathrm{X}]}{dt} = k[\mathrm{X}]^2. \tag{4.11}$$

If a plot of $\frac{1}{[\mathrm{X}]}$ versus time produces a linear graph, it would indicate that the reaction is second order [50]. The rates of reaction, as mentioned above, can be related to temperature. This forms the basis of the Arrhenius equation which is discussed in the next section.

In summary, the above equations can be simplified into

$$v = -\frac{d[\mathrm{X}]}{dt} = k[\mathrm{X}]^n, \tag{4.12}$$

where *k* is the rate constant and *n* is the rate order of the reaction.

4.1.3 Arrhenius equation

The relationship between the temperature and rate of reactions can be found by expressing the equilibrium constant as a function of temperature and heat of the reaction [51]. This is given by

$$\frac{d\ln \mathrm{K}}{dT} = \frac{-H}{R}, \tag{4.13}$$

where K is the equilibrium constant, H is the heat of the reaction and R is the universal gas constant .

The equilibrium constant is normally expressed as the ratio of the products and reactants and is given as the forward reaction over the reverse reaction and is expressed as

$$K = \frac{k_1}{k_2} = \frac{\text{forward}}{\text{reverse}}. \tag{4.14}$$

By substituting equation (4.14) into equation (4.13) we obtain

$$\frac{d\ln k_1}{d(\frac{1}{T})} - \frac{d\ln k_2}{d(\frac{1}{T})} = \frac{-H}{R}. \tag{4.15}$$

The above equation can be divided into two parts with the form

$$\frac{d\ln k}{d(\frac{1}{T})} = \frac{-E_a}{R}, \tag{4.16}$$

where E_a is the difference in energy of reactants and products and is the activation energy.

Taking E_a as constant and integrating results in,

$$\ln k = \ln A - \frac{E_a}{RT} \tag{4.17}$$

where ln A is the constant.

The above equation can be rewritten as

$$k = Ae^{\frac{-E_a}{RT}} \tag{4.18}$$

where A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature and E_a is the activation energy [51]. Equation 4.18 is referred to as the Arrhenius equation.

The pre-exponential factor (A) also called the frequency factor or the Arrhenius factor is related to the frequency of collisions between the molecules [52]. As the temperature of a reaction increases more molecules collide with greater frequency. The frequency factor is given by

$$A = \sqrt{\frac{T_f}{T_i}} \tag{4.19}$$

where T_f and T_i are the final and initial temperatures, respectively [53].

The activation energy (E_a) is the energy barrier that the reactants need to overcome in order to react and form products. E_a is expressed in units of J.mol^{-1}. Figure 4.1 illustrates the concept of activation energy in which the reactants (X and Y) need enough energy (E_a) to create the transition state (XY) and form products Z. The transition state is the state in which reactants form bonds prior to forming actual products [49].

By differentiating equation (4.18) we obtain

$$\frac{d\ln k}{d(1/T)} = -\frac{E_a}{R}. \tag{4.20}$$

A plot of ln k against $\frac{1}{T}$ gives a slope which equals $\frac{-E_a}{R}$. By substituting the universal gas constant. The activation energy can be obtained. Substituting the activation energy back into the Arrhenius

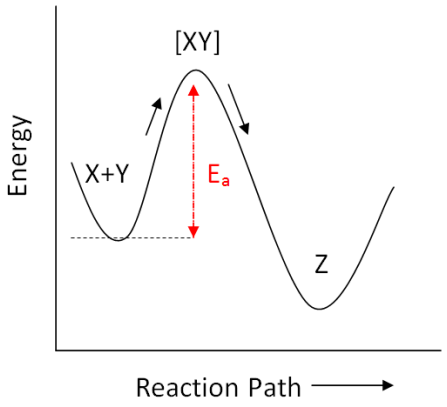

Figure 4.1: The energy of a reaction mechanism in equation 4.1 where E_a is the activation energy [49] .

equation gives the pre-exponential factor (A). These parameters can be used to find thermodynamics parameters such as activation free energy, activation enthalpy and activation entropy. These thermodynamic parameters will be discussed in the following section 4.2 [54].

4.2 Thermodynamic Properties

Having obtained a method to find the activation energy and the pre-exponential factor, we will now aim to identify thermodynamic properties using these results. The key thermodynamic properties of reactions are the activation Gibbs free energy (ΔG) change, activation enthalpy (ΔH) change and activation entropy (ΔS).
The activation enthalpy is a measure of the energy required for a reaction to overcome the transition state. The activation enthalpy is defined as

$$\Delta H = E_a - RT \tag{4.21}$$

and is expressed in units of kJmol^{-1}

The activation entropy relates to the probability of a reaction to occur and to the orientation of the molecules and the bulk (the greater portion of compound) composition [54].
The activation entropy is given by

$$\Delta S = R\ln A - R\ln(\frac{kT}{h}) - R, \tag{4.22}$$

where k is Boltzmann constant and h is Planck's constants which are 1.380 x 10^{-23} JK^{-1} and 6.626 x 10^{-34} J.s respectively. The activation entropy is in units of $J.mol^{-1}K^{-1}$.

The activation Gibbs free energy is the energy required for a reaction to occur and is given by

$$\Delta G = \Delta H - T\Delta S, \tag{4.23}$$

where the units are $kJmol^{-1}$. If the change in Gibbs free energy is positive then an activation energy is needed in order for the reaction to occur. If the change in Gibbs free energy is negative then the reaction occurs immediately after equilibrium [54].

Determining the different kinetic and thermodynamic parameters of the reactant species help in understanding more about the reactive species. The next section will aim to understand the interactions between atoms and surfaces.

4.3 Surface Physics

Surface physics is the study of chemical compositions and atomic arrangements at the surfaces of solids and the theory and observation of their mechanical, electronic and chemical properties [55]. Surface physics has become a important segment of solid state physics and has steadily developed over the years [56].

The surface concepts include adsorption, catalysis, oxidation, friction, adhesion and lubrication. The bulk properties include electrical and thermal conductance, melting point, heat capacity, modulus and hardness. The surface and bulk properties can differ from each other which provides physicists with the added motivation to study bulk and surface interactions [57].

In this section the main concepts associated with surface physics is discussed. The concept of deformation which plays a critical role in understanding the surface physics of the conductors and contaminants will be introduced. We finally aim to understand the copper sulphide formation using surface physics.

4.3.1 Definitions and Concepts

It should be noted that the surface interaction as discussed in this section will deal with a small amount of the top layers of the solid bulk.

The first definition that is significant in understanding surface physics is adsorption. Adsorption is the accumulation of atoms on a surface. The substances that are adsorbed on a surface is referred to as adsorbates. The surface at which the accumulation of adsorbates occur is the adsorbent or substrate. The reverse process of the removal of molecules from a surface is called the desorption process. Coverage is also an important concept in surface physics and is defined as

$$\theta = \frac{\text{Number of occupied adsorption sites}}{\text{Number of adsorption site present}}, \tag{4.24}$$

with units of area.

Another important definition is absorption (not to be confused with adsorption). Absorption is a mechanism that transports atoms through the surface and into the bulk.

Three common terms referred in this chapter are islands, vertical and lateral interactions and the sticking coefficient. Their definitions are given as follows [58]:

- Islands: Accumulation of adsorbates to form ”two dimensional crystallites”.
- Vertical Interaction: The interaction between the adsorbate and its surface.
- Lateral Interaction: The interaction within the adsorbed layer and between adsorbates.
- Sticking Coefficient: A value for the possibility that an adsorbed molecule will remain on the surface.

The definition of surface energy is the excess energy as compared to the bulk part of the solid. When an interaction occurs at a surface or more specifically when it leaves a surface, it results in dangling bonds being created on the absorbent. These dangling bonds have free valencies and still remain on the surface [59].

There are two main types of adsorption that can occur in solids, liquid or gases. These adsorption types are physisorption and chemisorption [60] which will be briefly discussed [61].

4.3.2 Physisorption

Physisorption occurs through a weak interaction (Van der Waals interactions) between the atoms and the surface. This adsorption reaction occurs when there is an exchange in charges between the adsorbate and the surface. The exchange causes mutually induced dipoles. A dipole is characterized as the separation of charges in opposite directions in molecules. When the adsorbate interacts with the surface, the dipole from one molecule will induce an electric field near a second molecule. This causes further charges variations on the second atom [62].

In physisorption, the structure and electronic properties of the atom and the surface involved is unchanged. This type of adsorption normally occurs at lower temperatures and this adsorption is normally reversible. It is possible that several layers may be formed on a surface with a small binding energy. The molecule that is physisorbed can depart the surface at any time. The energy for the atom to depart the surface is normally around a minimum of 20 kJmol^{-1} [60, 61].

In reactive species, physisorption is the first stage prior to chemisorption [58].

4.3.3 Chemisorption

Chemisorption involve chemical bonds taking place between the atoms and the surface. The most prevalent bond is the covalent bond. This type of adsorption involves the exchange of electrons between the different reactants. The potential energies for a chemisorption reaction are normally around 200 kJmol^{-1} greater than the physisorbed molecule . The bonds between the adsorbates and the surfaces are very strong and can only be broken at high temperatures. This type of reaction may also require an activation energy to allow the reaction to occur [61].

The chemisorption process involves the orbitals in reactive molecules to change when they interact with the surface. The change in the atomic orbital shell causes the formation of new chemical products [58].

An important factor in chemisorption is the influence of the absorbate on the work function. The change in the workfunction will be discussed in the following section.

Work function

The definition of the workfunction is the lowest energy required to detach an electron from the bulk solid to a "point" just outside the surface. In this dissertation we use the definition of the work function ($e\phi$) as the difference between the fermi level (E_F) and the vacuum energy (E_{vac}) state [58] . The fermi level is defined as the estimated energy for an electron that is located in the bulk.

The photo-electric effect experiment explains the work function by beginning with the bulk having the initial state called the ground state. Here, the bulk has an energy called E_N with N electrons. A detached electron leaves the bulk and travels just outside the surface. This electron is a free valence electron. The bulk now has an energy state of E_{N-1} since the number of electrons in the bulk is N-1. The work function at zero temperature is therefore given by [58]:

$$e\phi = E_{N-1} + E_{vac} - E_N. \tag{4.25}$$

At specific temperatures, the workfunction is described as the change in states using thermodynamics properties. The change of free energy F with regard to the change in electron number, $(\frac{\partial F}{\partial N})_{T,V}$, with T, V as constants, replaces the difference in energy states, $E_N - E_{N-1}$. $(\frac{\partial F}{\partial N})_{T,V}$ is called the electrochemical potential, μ of the electrons and is known as the Fermi level.

The work function is therefore given by [58]:

$$\begin{aligned} e\phi &= E_{vac} - \mu \\ &= E_{vac} - E_F. \end{aligned} \tag{4.26}$$

The atoms/adsorbates that are adsorbed onto a surface can change the electronic structure of the metal surface. The change occurs when charges continuously are exchanged between the surface and the adsorbate. This change influences the work function [58]. A change in the work function is a factor that causes reconstruction and relaxation of surfaces. Reconstruction of a surface is the change of the layers of a surface while relaxation of a surface is the change in the spacing between the layers.

Having discussed the influence adsorbates has on the surfaces work function, we now discuss the formation of layers on the surface.

4.3.4 Coverage

The accumulation of adsorbate layers is called the coverage and occurs through two processes. In the first process, a layer is formed when adsorbates distribute in a random distribution as illustrated in Figure 4.2. In the second process, a layer of adsorbates is formed when the adsorbates develop into an island that has a full first layer on the surface. The distribution of islands is illustrated in Figure 4.3. Investigations have shown that temperature influences the way coverage occurs [58]. Coverage layers interact through vertical and lateral interactions. In situations where the energy of the chemisorption process is high, the vertical interaction is larger than the adsorbate-to-adsorbate interaction

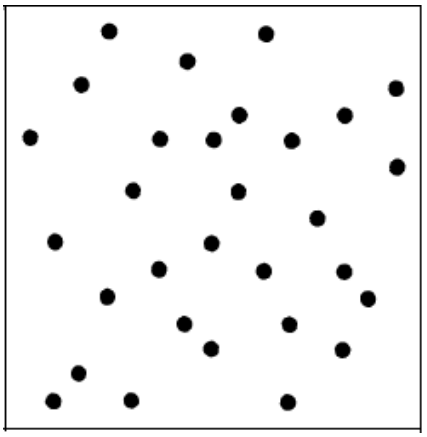

Figure 4.2: A random distribution of adsorbates on a surface [58]

The buildup of the layers of adsorbed molecules can occur by the following interactions [58]:

i) Van der waals interactions which is a precursor for the physisorption reaction and occurs due to changes in charges between the adsorbates and the surface.

ii) Dipole forces which occur due to the dipole moments of the adsorbed molecules. The dipole forces also exist because of the dipoles that are formed when the surface and molecules interact.

iii) The orbitals overlap in the atoms that are situated next to each other which results in mutual repulsion.

iv) A molecule that is strongly adsorbed can change the structure at the surface. The exchange

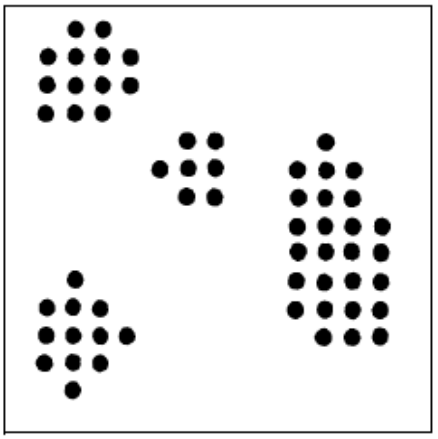

Figure 4.3: Islands of adsorbates on a surface [58].

in charges between the adsorbate and surface can cause another adsorbate to interact with the surface.

v) Alternatively, if a second adsorbate intends to interact with the surface, it will need to "do more work" in order to overcome the surface (adsorption) sites that have been filled by the previous adsorbates.

So far, we have discussed the concept of adsorbates interacting with the surfaces and the formation of layers and coverage. We now discuss the factor that influences the absorbate to remain on the surface. Investigations [58] have shown that the "sticking coefficient" plays an important role in influencing the absorbate to remain on the surface. The sticking coefficent (S) is the possibility of an adsorbate molecule remaining on the surface [58].

The key factors that cause an absorbate to remain on the surface is given as follows [58]:

a) The adsorbed molecules need to reach the activation energy given by E_a. The atoms that are greater than E_a will remain on the surface.

b) The sticking coefficient value needs to be a factor of the $exp(-E_a/kT)$ where k is the Boltzmann constant.

c) The orbitals of the adsorbate should be aligned in specific ways similar to the free bond orbitals on the surface.

d) Adsorbtion sites must be available so that adsorbates can interact with the surface in the first place. The more sites that are available, the more likely adsorbates will remain on the surface.

e) The adsorbate should exchange some of its kinetic energy with the surface.

The different concepts relating to the interaction of adsorbates and surfaces have been discussed. The following section will discuss the influence of the atoms on the surface and the deformation that occurs when adsorbates interact with the surface.

4.3.5 The adsorbate (sulphur) interaction with copper surfaces

Investigations have found that sulphur is the most commonly used atom to measure the interactions of adsorbates and surfaces. The understanding of sulphur compounds interacting with copper surfaces can also explain complex systems such as CO on Cu or C_4H_5N on Al (001) surfaces [63].

The following sections will discuss the theoretical research of sulphur and copper surface interactions. The interaction of S on a Cu(001) surface, illustrated in Figure 4.4, is the basic and the most non-reactive configuration. The grey atoms in Figure 4.4 represents the copper atoms while the yellow atoms represents the sulphur atoms .

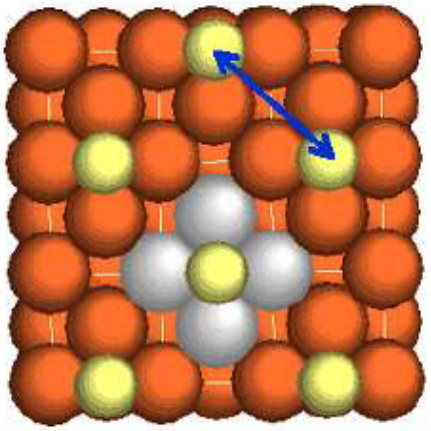

Figure 4.4: A 2x2 geometry of sulphur and copper. [63]

There are three different types of sites that adsorption can occur: bridge site, hcp hollow site and

fcc hollow site.

Bridge site

The bridge site is a point situated above the surface atoms. Surface relaxations (rearrangement of the surface) is significant when discussing sulphur interacting with copper since the relaxation influences the amount of layers formed on a surface. There is a correlation between the coverage and the adsorption energies [64]. The coverage decreases as the adsorption increases. The coverage is related to the surface lateral deformations and relaxations that occur when interactions occur. At the bridge site, the metal surface will buckle causing the atoms to move out and the bonding between the sulphur atom and two other atoms on the surface will occur. Driver and Woodruff et al. (as citied in [64]) also explains that buckling will occur when the sulphur atom is adsorbed on the bridge site of the surface.

Hcp and fcc hollow sites

The hcp (hexagonal close-packed) sites are normally situated in the second layer of atoms in the copper while the fcc (face centered cubic) sites are positioned in the third layer. The sulphur atom that is chemisorbed interacts with three copper atoms in the hollow sites. The atoms move further apart to allow the sulphur to be in the surface layer. The adsorption of the fcc hollow site is greater than the adsorption of the hcp hollow site since the sulphur atom does not feel the repulsive force from the second layer which will result in it moving closer to the surface layer [64]. The fcc and hcp sites are responsible for the adsorption of adsorbates on a surface. An example of the interaction between sulphur and copper surfaces are given below.

Research shows that sulphur is likely to interact in the four fold hollow site with a bond length of 2.26 Å [63]. A four fold hollow site is the site whereby all four atoms may touch the adsorbate. The interaction of the sulphur causes the Cu atoms to shift away from the adsorbate (sulphur). The copper atoms that are located on the surface layer may not move perpendicular to the surface. This causes the atoms below the surface layer to make space for the displacing copper atoms resulting in buckling in the surface. It was found that the bonding energy of a sulphur atom to a 2x2 fcc copper surface is 0.54 eV [63]. The copper to sulphur bond distance in the bridge site was found to be 2.31 Å while 2.33 Å at the fcc hollow site [64].

4.3.6 A quantum mechanical study of sulphur atoms on copper surfaces

In this section, we aim to understand the formation of copper sulphide based on the interpretation of the work done by Ferral et al. [65]. In their quantum mechanical study, they demonstrated that sulphur compounds are adsorbed onto a copper surface and were experimentally found to form self-assembled monolayers. The interaction of sulphur on the copper surface was seen to occur more readily in polycrystalline copper (clear uncontaminated copper) than already contaminated or unclean surfaces. A typical example of a sulphur-headgroup adsorbing onto a copper surface is given in Figure 4.5. This figure illustrates a theoretical model of 25 metal clusters where the interaction occurred at the FCC hollow site. An unpaired electron located in the surfaces orbital readily interacted with the absorbate (sulphur) free electron since the symmetry of the orbitals are the same. The sulphur therefore fitted comfortably in the copper cluster since they had a similar and correct electronic structure such that bonding can take place. If the reactants do not have the same orbital symmetry, interactions may occur however it would result in a small binding energy and consequently large activation energy.

The theory by Ferral et al. [65] agrees with our understanding of DBDS interactions with copper. The sulphur compound readily reacts with copper to form complexes which was identified by the increase in the rate constant of DBDS. X-Ray Adsorption Fine Structure (SEXAFS) testing was used by Ferral et al. [65] to investigate the surface change that occurred on copper surfaces. They identified that the reconstruction of the surface occurred in the first monolayer of the surface. Ferral et al. [65] thereafter used a cluster model method to investigate the chemisorption of the sulphur adsorbate onto the copper surface. It was predicted effectively that if the atoms had the correct electronic structure then the binding energy can be calculated. Ferral et al. [65] also predicted that adsorbates introduce relaxations on the surface, however, they do not change the chemical bonds between the interactions.

Ferral et al. [65] also concluded that the sulphur that was adsorbed onto the surface caused reconstruction in the first layer of the surface. The heating of the copper surface that had a monolayer of sulphur caused the sulphur atoms to desorb (leave) from the surface. It was also found that as the coverage of the adsorbate was increased then the binding energy decreased. They also observed that interactions can occur in both bridge sites and hcp hollow sites. Using their cluster model method, they identified that the sulphur that was perpendicularly adsorbed onto the surface, had a binding energy (BE) of -43 kcal/mol^{-1} (approximately equal to -180KJmol^{-1}) and occurred at a

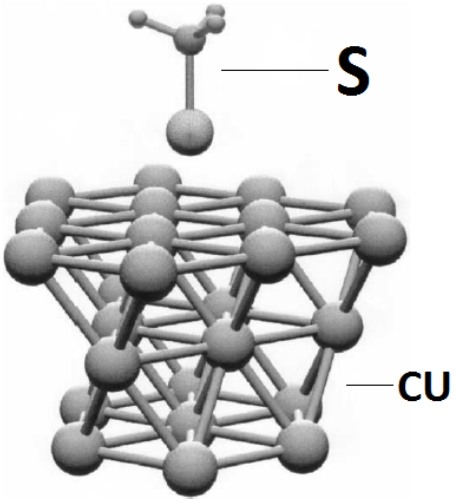

Figure 4.5: Sulphur atom interacting in the hollow site of the copper cluster model [65].

bond distance of 1.9 Angstroms.

Having discussed the basic considerations with regard to surfaces and adsorbates, we will bring the focus back to explaining more about transformers and a key component in transformers that experience the biggest effect from the kinetic and surface physics considerations.

Chapter 5

Insulation System of transformers

5.1 Introduction

The biggest effect of corrosive sulphur is its ability to cause failure in transformers. It has been identified that the failure of transformers occur when the solid (kraft paper) and liquid insulation (oil) breaks down. This chapter deals with understanding the breakdown in liquid insulation. More research is dedicated to investigating the insulation system as compared to other components in the transformer such as the core and windings [66].

The failure of the insulation system in transformers ultimately results in the failure of the whole transformer system. The operations of the insulation in the transformer system is not always found by routine testing but rather by using accelerated testing. Accelerated testing are tests performed in temperatures higher than the normal operating temperatures. This is done to predict the lifetime of the transformers and the expected breakdown of the transformer system [66].

Power transformers create a large amount of heat through electrical, mechanical and thermal stresses. Transformers therefore need to have both solid and liquid insulation which distribute or dissipate the heat through cooling. The success rate of a transformer is dependent on the life of the insulation system. The solid and liquid insulation are responsible for the dielectric strength of transformers [20]. Electrical engineers define the dielectric strength as the ability of the transformer to withstand electrical stresses without failing [1]. The combination of the solid and liquid insulation is the main component of the transformer that is irreplaceable and the most likely to be affected by loading conditions of the transformers [20]. The degrading of the transformer oil can cause electrical components of the transformer to malfunction. By products, such as acids and

sludge, form and deposit in various parts of the oil. This results in the dielectric and heat transfer properties of the oil to be effected [1].

5.2 Liquid Insulation

The liquid insulation consists of the transformer mineral oil which is a dielectric fluid refined from crude oil [1]. The different types of oil are dependent on the manufacturers specification and can include high amounts of naphthenic and paraffinic compounds and a small amount of aromatic and polyaromatic compounds. It is said to be weakly polarized due to the mixture of the hydrocarbons [67].

Mineral insulating oil has the property of low viscosity which allows the oil to form convection currents to transport the heat away from the core and windings and subsequently cooling the system [20].

Over time and due to the influence of aging factors the properties of oil can change. This change was found to be affected by the water and oxygen content present in the oil and also by the presence of contaminants [1]. These contaminants are normally the by-products of chemical reactions that take place and dissolve in the oil or can be additives [43]. The by-products cause problems with the overall transformer insulation since they are semi-conducting [43, 68]. The end products of the interactions of by-products are acidic and are found to affect the electrical components of the transformer as well as the solid cellulose insulation. The acids that are deposited on the fibers, distort the fibers and metal parts in the transformers [20].

Liquid insulation have specific functions which aid the transformer. There are four significant functions of the liquid insulation:

- The oil acts as a dielectric medium that prevents electrical conductivity and it has a high dielectric strength [1, 17, 18].
- The oil serves as a heat transfer medium by transferring heat from the core and windings and dissipates heat into the surroundings [1, 69, 70].
- The condition of transformers are normally assessed by testing the oil from the transformer [1, 70, 71]. Therefore it is used as as diagnostic tool.

- The oil transports heat and sludge away from the solid insulation and thus functions as a protection for the solid insulation [1, 17, 18].

5.3 Electric Properties of transformer oil

The different electrical characteristics of transformer oil include the dielectric strength, conductivity and dielectric constant. In this section, we discuss the various properties of oil as a dielectric medium.

5.3.1 The oil as an dielectric medium

The main property of oil as a dielectric medium is its ability to prevent the flow of charge and insulating the whole transformer system. It also becomes polarized when an electric field is applied [62].

The theory of dielectric materials begins by understanding the idea of dipoles in liquids. A dipole (**p**) can be characterized as the separation d of charges q in opposite directions and results in equation 5.1.

$$\mathbf{p} = q\mathbf{d} \tag{5.1}$$

Dielectric insulating oil can exhibit properties of being both polar and non-polar [62, 69]. Polar molecules in the oil have electrical charges already separated from each another. One end of the molecule has a positive charge while the other end has the negative charge. Non-polar molecules that are in the oil do not have an existing electric dipole. The molecules will only experience an electric dipole when it is placed in an electric field.

5.3.2 Polarization and the dielectric constant

When a material is placed in an electric field, it becomes polarized. Polarization is the movement of positive charges in the direction of the electric field and the negative charges in the opposite direction of the electric field. If the molecules in a dielectric are held together by weak bonds, the electric field causes the molecules to realign themselves to the electric field . An important characteristic of a dielectric is therefore the ability to be easily polarized. This polarizability is

quantified as the dielectric constant of a medium.

For a more complete discussion of the equations used below see references [62, 72], we discuss the essentials.

The relationship between the dipole moment (**p**) and the electric field (**E**) is given by.

$$\mathbf{p} = \alpha \mathbf{E}, \tag{5.2}$$

where α is the atomic polarizability. The total charge density ρ in the dielectric medium is the sum of the free charge density ρ_f and the bound charge density ρ_b given as

$$\rho = \rho_b + \rho_f. \tag{5.3}$$

From Gauss's law written in differential form we have

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}, \tag{5.4}$$

where ε_0 is the permittivity of free space which will be explained later.

The bound charge density ρ_b is the effect of the polarization on the charges and is given by:

$$\rho_b = -\nabla \cdot \mathbf{P}, \tag{5.5}$$

where **P** is the polarization.

Substituting equation (5.5) and (5.4) into equation (5.3), we obtain the following equation :

$$\varepsilon_0(\nabla \cdot \mathbf{E}) = -\nabla \cdot \mathbf{P} + \rho_f, \tag{5.6}$$

which simplifies to

$$\rho_f = \nabla \cdot (\varepsilon_0 \mathbf{E} + \mathbf{P}), \tag{5.7}$$

where

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \tag{5.8}$$

is called the electric displacement. The polarization is directly proportional to the electric field and related by the equation

$$\mathbf{P} = \varepsilon_0 \chi_e \mathbf{E}, \tag{5.9}$$

where χ_e is the electric susceptibility.

By substituting the equation for the relationship between the electric field and polarization given in equation (5.9) into equation (5.8), we obtain:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \varepsilon_0 \chi_e \mathbf{E} \tag{5.10}$$

$$= \varepsilon_0 (1 + \chi_e) \mathbf{E}. \tag{5.11}$$

The electric displacement can be rewritten in compact form

$$D = \epsilon \mathbf{E}, \tag{5.12}$$

where $\epsilon = \varepsilon_0 (1 + \chi_e)$ is defined as the permittivity of the dielectric medium.

The dielectric constant which is also referred to as the relative permittivity is defined as,

$$\varepsilon_r = (1 + \chi_e) = \frac{\epsilon}{\varepsilon_0}. \tag{5.13}$$

The dielectric constant and dielectric strength (which will be explained in the next sub-section) describe the dielectric properties of the transformer oil. The physical and chemical properties of oil is summarized in Table 5.1 [69, 73].

5.3.3 Dielectric strength

Dielectric strength is another important property of insulating oils. The dielectric strength is the lowest electric field that would cause the dielectric medium to allow the flow of charges. The dielectric strength of the medium is the ability of the transformer to withstand the electric stress on the insulation system [1]. The testing procedure for the dielectric strength test is given in section 6.3.4.

Table 5.1: The physical, chemical and dielectric properties of transformer oil and the typical values for non contaminated transformer oils [73].

	Units	**Typical Values**
	Physical Properties	
Colour	HU	Max 200
Appearance		Clear with no contaminants
Density at 20 °C	kg/dm^3	Max 1.00
Kinematic Viscosity at 40 °C	mm^2/s	Max 35.0
	Chemical Properties	
Water Content	mg/kg	Max 200
Neutralization or acid number	mg KOH/g	Max 0.03
Oxidation Stability :		
Total Acid content	mg KOH/g	Max 0.3
Total Sludge content	% Mass	Max 0.01
	Dielectric Properties	
Breakdown Voltage	kV	Min 45
Dielectric Dissipation Factor		Max 0.03
Voltage Resistivity	G ohm m	Min 2

5.3.4 Conductivity

Dielectric conductivity in transformers shows the ability of the dielectric to behave as an insulator or conductor [69]. Dielectric fluids can be described as liquids that have a small self dissociation of ions. This means that free ions are not readily formed in the oil. The dielectric fluid, as already mentioned, can be classified according to being polar or non-polar. The fact that there could be permanent dipole moments results in there being intermolecular interactions in the oil [69].
When a low electric field is applied dissociation of ions occur. When the electric field is increased, a current change is observed in the oil. Saturation occurs when a medium electric field is applied and the current slowly approaches the breakdown area . Figure 5.1 shows the conduction current against the different electric fields. It illustrates that ionic interactions occur at low electric and current fields while saturation occurs at a medium electric and current fields. The field aided section in the graph is formed due to an applied cathode (which increases the current and electric field) in order to understand the effect of the current at high electric fields [67, 71].

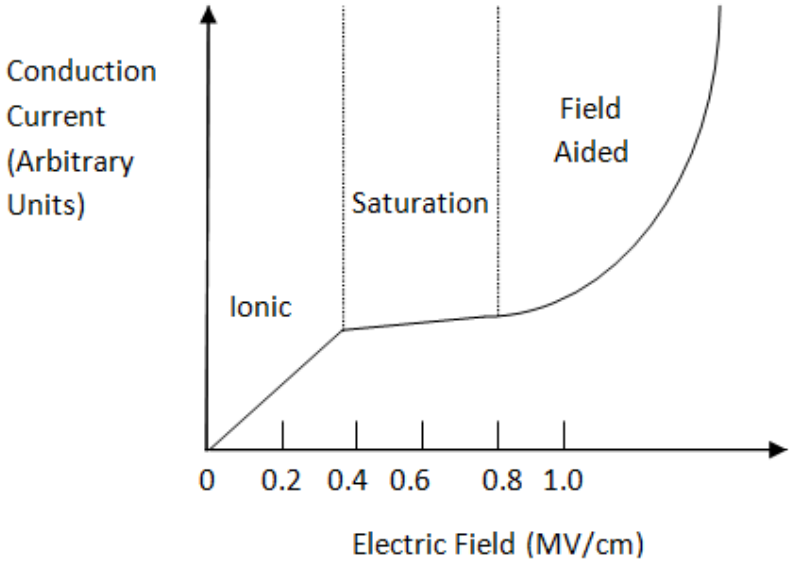

Figure 5.1: The conduction current versus the input electric field [67].

5.4 Breakdown of the liquid insulation

Electrical breakdown of an dielectric material occurs when the material can no longer provide adequate insulation to a system. This primarily occurs when the obstruction preventing the flow of electric current is broken [69]. Sometimes the oil can recover from a breakdown, however, a chemical change does occur internally that reduces the lifetime of the oil [69]. The majority of dielectric liquids are contaminated with impurities. Voltages applied to the dielectric liquid would cause the solid impurities to become polarized and charged. The charged and polarized impurities line up to 90 degrees to the equipotential surfaces [71, 74].

The electrical breakdown of insulating liquids is normally explained using two theories namely, the electronic breakdown theory and the suspended particle theory. Excessive stress and heating applied to dielectric fluids causes an increase in collisions of molecules. These collisions results in an energy and heat transfer between molecules. The heating and stress can breakdown particles to form ions. A collection of ions create paths of electrical charges referred to as streamers. These 'harmful' paths induces arcing which results in the ultimate failure and breakdown of the oil [69, 71].

The latter theory describes the development of contaminants which are influenced by the electric field. The contaminants become charge and react with other molecules in the dielectric liquids and creates solid deposits. The solid deposits changes the physical properties of the oil [71].
The research in conduction mechanisms and the breakdown is highly significant not only to understand when breakdown is meant to occur but also to understand the different properties of the oil to extend it usage. To complete this section on insulation, we briefly discuss solid insulation.

5.5 Solid Insulation

Solid insulation in transformers consists of Kraft paper. This kraft paper consists of 90 % main cellulose, 6-7 % other forms of cellulose and 3-4% other compounds [75]. This composition of paper is used since it is cost effective [76]. Insulation paper is wrapped around the copper windings and between 30 to 120 μm thick [75]. The expected lifetime of solid insulation is about 20 years [77] and its dielectric constant is 4.4 [76]. The biggest disadvantage to using solid insulation is that when the paper fails it cannot repair itself and the ultimate failure of the transformer normally occurs [78]. The cellulose molecules that make up the paper are held together by glycosdic bonds illustrated by Figure 5.2. Therefore the cellulose component of the paper consists of chains of glucose molecules. The average length of the glucose chains is called the Degree of Polymerization (DP). The DP for new kraft paper in a transformer is 950 while the DP value for degrading paper is 200 [78].

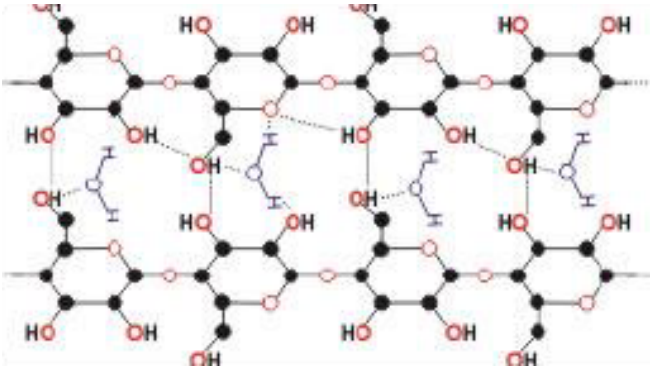

Figure 5.2: The glucose molecules joined together by glycosdic bonds to make up the cellulose [79].

The breakdown of the solid insulation are both due to high temperature or through contamination by products. The breakdown of the cellulose cause the glycosdic bonds to breakdown and release glucose molecules into the oil. These glucose molecules change into a compounds called furfurals. The furfurals also called furanic compounds can be identified through oil testing. The main type of furanic compound is called the 2-furaldehyde illlustrated in Figure 5.3 while the others are 5-methyl-2-furaldehyde, 5-hydroxylemethyl-2-furalhyde, 2-acetyl furan and 2-furfural alcohol [77, 78].

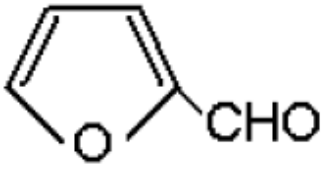

Figure 5.3: A derivative of the furanic compounds called 2-furaldehyde [75].

The basic understanding of all the theoretical factors in this thesis has now been discussed. The information that will follow will include the experimental setup and our own research.

Chapter 6

Materials and Methods

This chapter deals with the experimental setup and experimental procedures used. The discussion revolves around the specifications of the transformer, the setup of the experiment and the uniqueness of this experiment as compared to previous studies [3, 34, 38, 40, 43] regarding corrosive sulphur testing.

Research in corrosive sulphur is normally performed using accelerated aging tests. These tests involve immersing a copper strip and transformer oil in a test vial and applying different conditions, such as heating and nitrogen, to the test vial [40, 43]. The accelerated aging tests are normally performed in laboratories. The copper strip is then analyzed using the corrosive sulphur test.
Current research in corrosive sulphur struggles to obtain effective results since the research is performed in laboratories and not on a transformer in service. In a laboratory the oil is not subjected to the range of conditions that are present in an actual operating transformer.
The novelty of the research presented in this dissertation is that data was obtained from a fully functioning transformer under varying temperature conditions.

6.1 Experimental Setup

The experimental layout was designed and installed with the assistance of the eThekwini Electricity Department. The experiment is housed at the eThekwini Electricity Workshop located in Springfield, Durban. The experimental setup is illustrated in Figure 6.1. The experimental setup consisted of two three-phase 100 kVA distribution transformers. Both transformers are oil-filled with a high voltage to low voltage ratio of 11 kV: 400 V. Each transformer holds a current ratio of 5.24 A : 144 A and a frequency of 50 Hz . Transformer A had an impedance of 2.76 $\%$ while

transformer B had an impedance of 3.10 %.

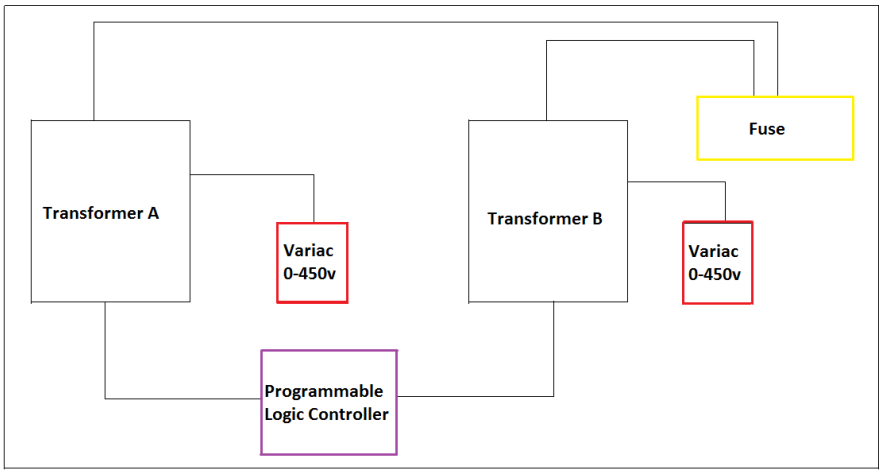

Figure 6.1: The experimental layout with two transformers, two variacs, a PLC and a fuse.

The transformer loading voltages are controlled by variacs which allows the voltage to be changed between 0 to 450 V. Both of these transformers are connected to a programmable logic controller (PLC) which allows periodic measurements to be logged and other factors such as temperature and humidity to be recorded. As a safety precaution both the transformers are connected to a fuse that breaks the circuit when the transformer fails. The fuse is shown in Figure 6.2.

Transformers A and B have the same components as shown in the Figure 6.3. The low voltage is located on the left side of the transformer and includes a short circuit line to allow the rated current (the current needed to prevent overheating) to be applied. The right side of the transformer has the high voltage bushings with a voltage of 11 kV. The sampling tap was located at the bottom of the transformers and the tap changer is situated in the middle of the transformers. The transformers also contain a breather located at the top left hand corner of the transformer as indicated in Figure 6.3. The breather contains silica gel that removes moisture from the air that is absorbed into the transformer when the transformer oil expands. Initially the silica gel was orange in colour, however, during the experiment the gel was observed to be turning blue. The blue colour signifies that moisture has been absorbed from the transformer. A heating lamp is located on the right side of the transformer. The importance of the heating lamp will be explained in the experimental procedure section.

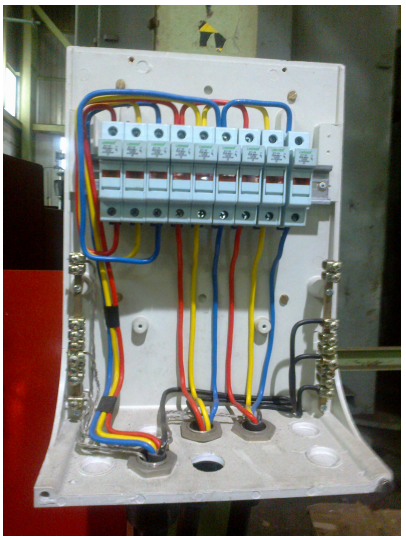

Figure 6.2: The fuse box connected to the transformer was designed to trip if the transformer fails.

Other important specifications of the transformers are:

- Both transformers have a cooling system of ONAN (Oil Natural and Air Natural).
- Each transformer has a total mass of 860 kg and an oil capacity of 375 L.
- The transformers were manufactured by Transformer Trend Technology CC in 2007.

The electrical layout is shown in Figure 6.4 and the final experimental setup is shown in Figure 6.5.

Figure 6.5 shows the actual experimental setup consisting of two transformers connected to a programmable logic controller. The transformer on the left (transformer A) and the transformer on the right (transformer B) initially contained clean insulating oil. Transformer B was the only transformer from which oil samples were retrieved for testing as it was in this transformer that contaminated oil was subsequently added. The testing of the oil samples was performed by Transformer Chemistry Services (TCS) [1]. A summary of the oil tests performed by TCS are given in section 6.3.

Both transformers operated at the typical current (rated current) calculated from the voltage found in equation 6.1. The rated current is the current that would not cause overheating, as mentioned before, or failure of the transformer. The rated current was achieved by short circuiting the sec-

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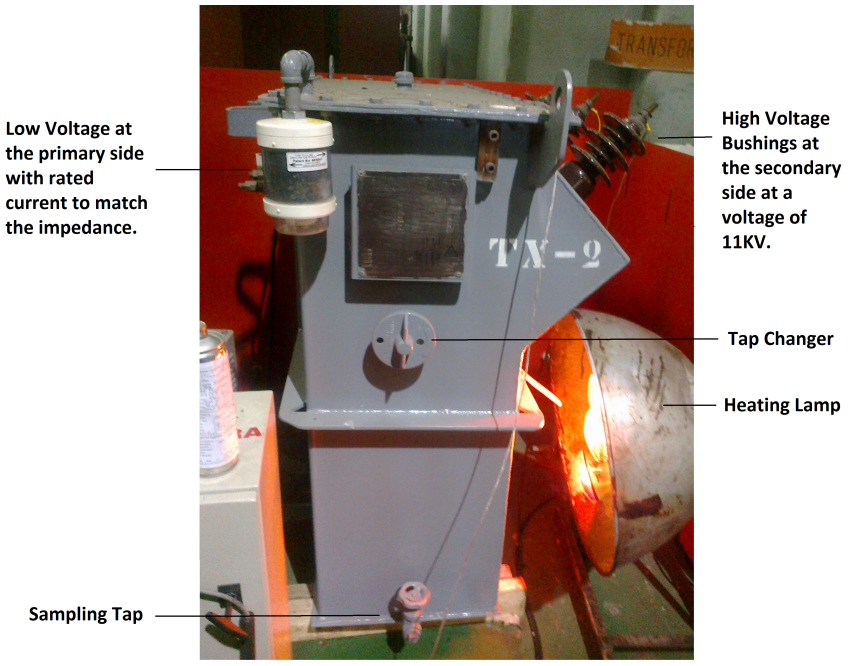

Figure 6.3: Transformer B illustrated with the different components.

ondary 400 V line of transformer B while a specific voltage was applied to the 11 kV line.

The specific or calculated voltage (V_{scB}) that was applied to transformer B to prevent overheating is given by,

$$V_{scB} = V_{rated} \times Z\%. \tag{6.1}$$

By using the transformers impedance (Z) of 3.10 $\%$, the V_{rated} of 11 kV, V_{scB} was found to be 341 kV.

6.2 Experimental Procedure

The oil in Transformer B was contaminated by adding 20L of oil that contained DBDS. Prior to the transformers being switched on, 500 ml testing samples of oil were taken from both the transformers. Tests were thereafter done by Transformer Chemistry Services (TCS) which showed that both transformers contained non-corrosive transformer oil. This test is called the corrosive sulphur test which is explained in section 6.3. It is important to note that even though the oil containing DBDS was added to transformer B, it was not detected by the Corrosive Sulphur test. Both of the

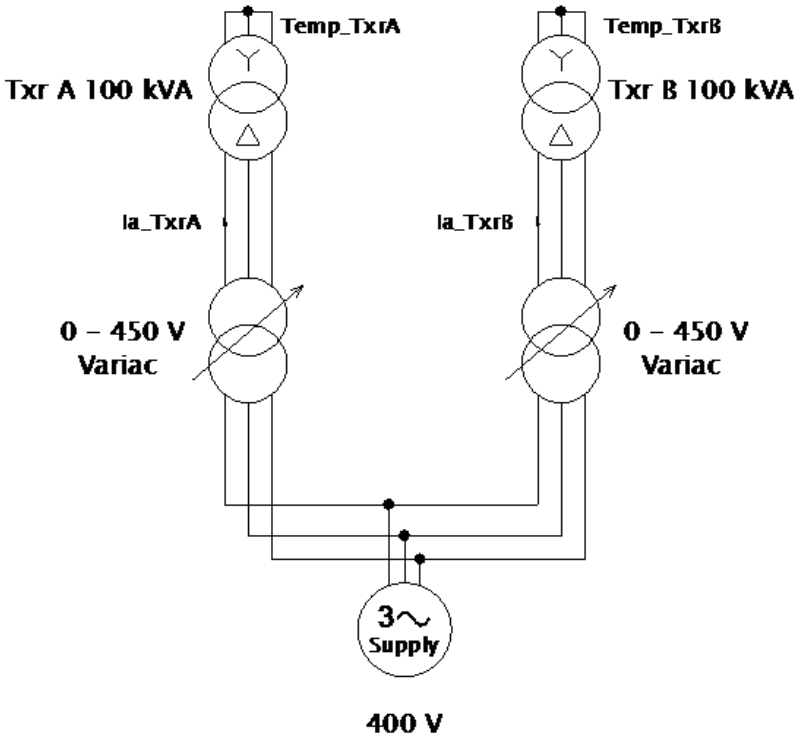

Figure 6.4: The proposed setup of the experiment with the two transformers and two variacs.

transformers were thereafter switched on. Transformer A was set at a maximum load current of 120 A which produced a maximum temperature of 60 °C.

The following experimental procedure pertained to Transformer B which was the transformer used in the rest of the experiment.
Transformer B was set at 0 % load and allowed to reach equilibrium in two days. An oil sample, the temperature, current and voltage measurements were taken after the transformer temperature was stabilized. The load was then increased to 25 % and the temperature allowed to stabilize. The current needed to increase the load by 25 % increments is given in Table 6.1. An increase in current lends to an increase in temperature.

When the maximum load and temperature of transformer B was reached, a method to further increase the temperature was needed. A heating lamp, illustrated in Figure 6.3, on the right side of the transformer, was introduced to further increase the temperature.
Oil samples were taken when the transformer was stabilized and the voltage and ambient temper-

Figure 6.5: The experimental setup that consists of two transformers and a logic controller to log the results.

atures were also recorded.

It was identified, through the analysis of the initial test results that the concentration of DBDS in the transformer oil was very low. The oil in transformer B was then replaced with oil from a running municipality transformer that had already been identified as being corrosive. This oil failed the corrosive sulphur test and was measured to contain 150 ppm of DBDS. The procedure was again performed with the samples of oil taken at 24 hour intervals for five days for three different temperatures.

6.3 Oil tests

This section describes various oils tests performed on the oil samples. All these tests are standards that were designed by the International Electrotechnical Commission (IEC) [11]. The IEC is an organization who approves methods for testing and other technological inventions.

Table 6.1: The current required to obtain the specific load percentage in transformer B.

Current (A)	Load
40	25 %
80	50 %
120	75 %
140	100 %

6.3.1 Corrosive Sulphur

The Corrosive Sulphur test was by far the most important test used in this thesis. This test, also called the ASTM D 1275B test, is a standard method formed by the American Society for the Testing of Materials (ASTM). The corrosive sulphur test, which is depicted in Figure 6.6, involves submerging a polished, bent, 6mm x 25 mm copper strip in 250 ml transformer oil contained in a flask. The flask is heated at 150°C for 48 hours. After heating, the copper strip in the flask is analyzed and compared to Table 6.2 or Figure 6.7 on page 67. Table 6.2, illustrates and provides a quantitative description of the level of corrosion by observing the colour of the copper strip. Figure 6.7 illustrates the degrees of corrosion with the left side being the least corrosive while the right side is the most corrosive copper strip. If a sample was not corrosive, the results normally display: Non-Corrosive 1A [11, 38].

6.3.2 Dibenzyl Disulphide

This test, given by the IEC as the IEC 60666 test, is called the Dibenzyl Disulphide test. The Dibenzyl Disulphide test measures the concentration of DBDS in the oil using Gas Chromotography with an Electron-Capture Detector (GC-ECD) [80, 81]. Gas chromatographs (GC) use gas to separate different compounds from a sample [81]. A sample of transformer oil is injected into the column of the GC. This column contains a liquid composition similar to the oil sample. A carrier gas, Helium (He), carries the sample of oil through the liquid mixture in the column. The liquid mixture slows down the compounds that are similar to the sample. The different compounds from the sample leaves the column at different rates and is measured separately. The DBDS compounds collect at the end of the column [80].

The DBDS sample collected from the GC test is bombarded with electrons which is measured by

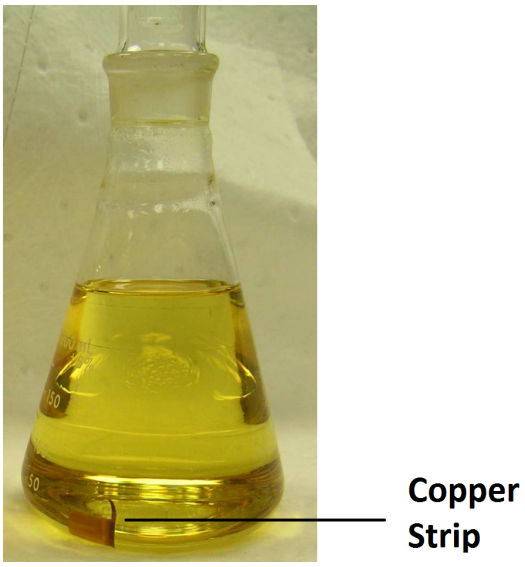

Figure 6.6: The ASTM D 1275B test containing the transformer oil and copper strip in a flask [38].

an Electron-Capture Detector (ECD). The ECD produces a graph of counts versus time which also shows the concentration of DBDS.

6.3.3 Interfacial Tension

The interfacial tension test determines if there are contaminants and by-products in the transformer oil. The instrument that is used to measure the interfacial tension is a tensiometer, which is illustrated in Figure 6.8 and follows the Du Noüy method. The Du Noüy method uses a ring to measure the force needed to rupture an oil-film and water interface [82]. A specific amount of oil is placed directly on a small amount (strip) of water. A platinum ring is placed below the oil-water surface. The ring is then pulled upwards and the force required to leave the oil-water film is recorded as the interfacial tension. The units of the interfacial tension are mN/m [84]. Clean oil has an interfacial tension value between 40 mN/m to 50 mN/m. Interfacial tension has an inversely proportional relationship to the amount of contaminants in transformer oil [84].

6.3.4 Dielectric Strength

The Dielectric Strength test measures the ability of the oil to continue to carry out its function when it experiences electrical stresses [82]. The test consists of two electrodes submerged in

Table 6.2: The copper strip is compared to this table to determines if the oil is corrosive [38].

Category	Degree	Colour Description
Non-Corrosive	1a	Light orange, similar to the copper strip
Non-Corrosive	1b	A dark orange
Non-Corrosive	2a	Claret Red
Non-Corrosive	2b	Lavender
Non-Corrosive	2c	Lavender, blue, silver and claret red
Non-Corrosive	2d	Silvery
Non-Corrosive	2e	Brass and gold
Non-Corrosive	3a	Magenta and Brassy colour
Non-Corrosive	3b	Red with green but no gray
Corrosion	4a	Dark gray, brown and light green
Corrosion	4b	Graphite black
Corrosion	4c	Glossy and black

transformer oil where a controlled voltage is released in the oil. When arcing occurs, the voltage is recorded and this is the dielectric strength of the oil [13]. The cleaner the oil, the higher the dielectric strength. The greater the dielectric strength the less contaminants are present in the oil. The ASTM standard name for this test is either ASTM 877 or IEC 156 [1, 82].

The experimental setup is given in Figure 6.9 and is used for the dielectric strength test. It consists of two electrodes 2.5mm apart that apply a voltage of 100kV. The arcing voltage is recorded for 5 measurements and the average value is the dielectric strength of the transformer oil [13].

6.3.5 Water Content

The water content in transformer oil is found using the Karl Fisher Titrator test. The IEC standard name for the water content test is IEC 60814. A sample of oil is added to a Karl Fisher test set and reagents are added automatically until the endpoint is reached. The units of the water content is recorded as mg/Kg [1].

Figure 6.7: The standard given by the ASTM which shows the different degrees of corrosivity [38].

6.3.6 Furan Analysis

The furan analysis test is required to identify the types and amount of furans in the oil. The procedure to perform the furan analysis is as follows: The transformer oil sample is passed through a solid phase extractor. HPLC (high performance liquid chromatography) analysis is performed on the extracted mixture. The furan compounds are thereafter separated and are normally identified using an ultraviolet detector. The quantity of furans is then recorded [85]. The following Table 6.3 [86] illustrates the furan content values and the significance of the amount of furans.

Table 6.3: Furan analysis amount with their respective condition status

Concentration of furans (ppm)	**Signficance of the data**
0-0.1	Healthy Transformer
0.1-1.0	Moderate Deterioration
1-10	Extensive Deterioration
>10	End of life Criteria

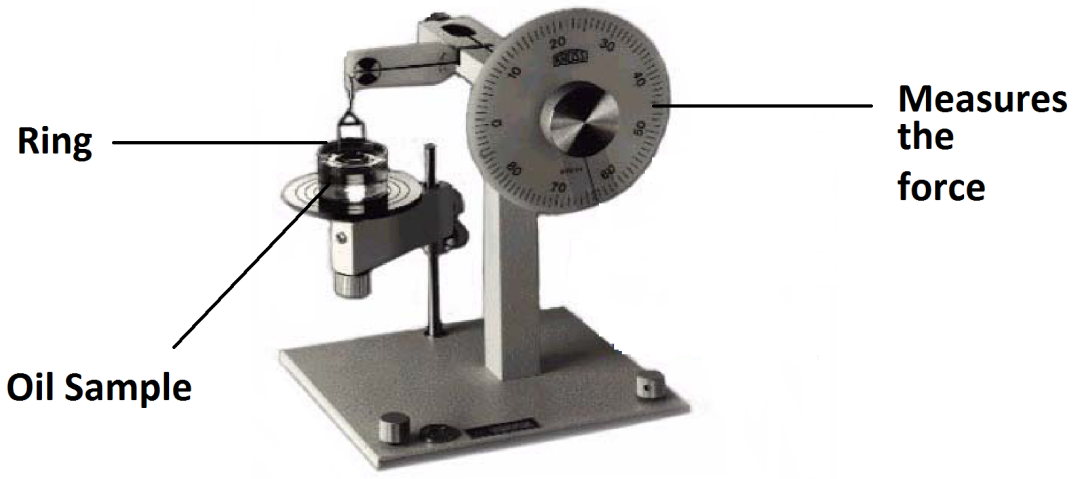

Figure 6.8: A tensiometer used to measure interfacial tension of transformer oil [83].

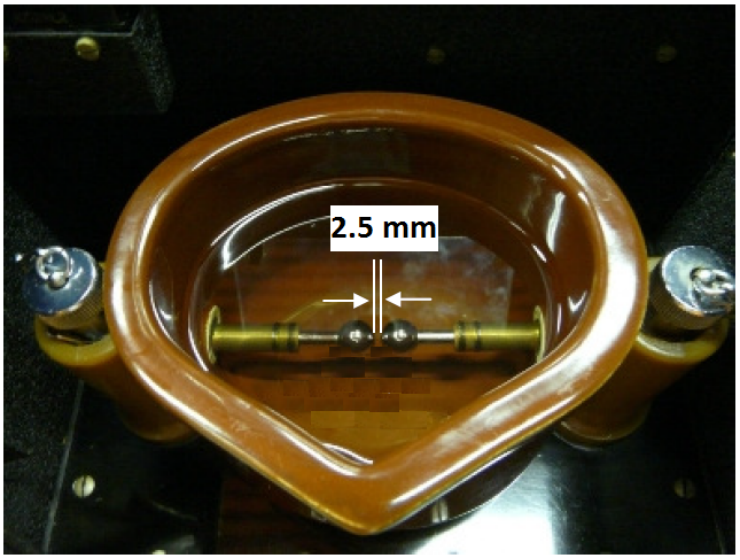

Figure 6.9: The dielectric strength experimental setup with two electrodes [13].

6.4 Tracking the copper sulphide deposition

The evidence of copper sulphide can only be found through identifying the corrosion of the copper conductors. However, the copper conductors cannot be removed from a fully functioning transformer. Another option to determine the concentration of copper sulphide would be to measure the amount of copper sulphide in the transformer oil. However, the amount of copper sulphide in the oil may not correspond to the severity of corrosion on the copper conductor.

The copper sulphide will only be present in the oil due to being desorbed from the copper conductor and leaked into the oil via broken kraft paper. As previously mentioned, the deterioration or distortion of the insulation paper causes the production of products called the furanic compounds. The experimental testing will focus on the testing of the furans to identify the severity of the copper sulphide deposition.

The next section will discuss and analyze the results obtained from this study. The following needs to be kept in mind throughout the discussion and analysis of results. The temperatures that are used in the data analysis are the temperatures of the transformer oil at the time when the samples were taken and not the temperatures when the samples were tested. It also needs to be noted that another aim of the experiment was to identify the amount of copper sulphide in the transformer, however, this is only possible if the windings are removed and analyzed for copper sulphide. In our experiment the windings were not removed from the transformer and the corrosive sulphur test indicated the corrosivity of sulphur and not the presence of copper sulphide particles in the oil. The presence of copper sulphide was instead tracked by the presence of DBDS and the concentration of Furans. The assumption that is made before the analysis of the results is that the reaction of DBDS results in the presence of copper sulphide.

Chapter 7

Results and Discussion

This chapter deals with the analysis of results that were obtained from tests performed on the different oil samples mentioned in the previous chapter. The analysis that were performed on the DBDS concentration results are based on the kinetic factors mentioned in Chapter 4.

7.1 Experimental Results

The oil samples obtained from the experimental setup was analyzed using the various oil testing methods described in the previous chapter. The most significant test, in the experimental setup was the Dibenzyl Disulphide test. The Dibenzyl Disulphide test indicated that that the initial concentration of DBDS in the transformer oil was 0.1 ppm. This concentration was determined by TCS, as mentioned previously, and remained constant at 0.1 ppm for a period of three days. It was concluded that the development of DBDS was slow and therefore an extended period was allowed to elapse (approximately 22 days) before the next set of samples were taken. However, the concentration of DBDS remained the same even after a period of 600 hours.

The low DBDS concentration did not however prevent other properties of the transformer oil from increasing or decreasing. The full first set of results for the experimental setup are illustrated in Table 7.1. It shows the furan concentration, water concentration, dielectric voltage test results that had significant changes. The DBDS and corrositivity of the oil were the only factors that did not change in the first part of the experimental results. The increase in furan concentration, water concentration and dielectric voltage, could be interpreted as being due to the degradation of the solid insulation as the temperature of the transformer was increased and not by the changes in the DBDS concentration.

Table 7.1: The full first set of experimental results obtained with the DBDS concentration remaining at 0.1 ppm and IFT being the interfacial tension.

Sample Time (hrs)	DBDS (ppm)	Furan (ppm)	IFT (mN/m)	Dielectric Strength (kV)	Water (mg/Kg)
0	0.1	0.09	23	37	43
24	0.1	0.08	23	33	33
48	0.1	0.12	23	31	52
528	0.1	0.1	23	16	75
552	0.1	0.18	22	23	90
600	0.1	0.27	22	15	119

As evident, from Table 7.1, the oil remains non-corrosive. However, the concentration of water increased steadily to a concentration of 119 mg/Kg for the 600 hours of the experiment. The excess water is the first indication that the oil and paper insulation is degrading. The furan concentration identifies the condition of the insulation paper. The maximum furan concentration of only 0.27 ppm in 600 hours of testing demonstrates that contaminants have not yet effected the insulation system of the transformer. The percentage error for the different test measurements are supplied by TCS and are illustrated in Table 7.2.

Table 7.2: Experimental errors for the test values.

Test	Error
DBDS	8%
Furans	5%
Water	10%
Dielectric Strength	20%
Interfacial Tension	5%

In the next set of measurements, the oil from transformer B was replaced with oil from a running transformer that was already identified as being corrosive. Initial sampling at ambient temperature

was done before the transformer was switched on. The results for the initial sampling done on this oil is indicated in the first row of Table 7.3. The temperature of the transformer oil fluctuated during the experiment and therefore the average temperature with the error was determined and is illustrated in the first column of Table 7.3.

Table 7.3: Full experimental results for the corrosive oil.

Temperature (°C)	**Sample Hours (hrs)**	**DBDS (ppm)**	**Furans (ppm)**	**Dielectric Strength (kV)**	**Water (mg/Kg)**	**IFT (mN/m)**
Room	-	66.3	0.21	18	41	20.0
37± 3	0	56.20	0.29	44	32	20.0
37± 3	24	43.60	0.23	47	34	20.1
37± 3	48	42.00	0.30	47	34	20.1
37± 3	72	53.80	0.26	53	37	20.1
37± 3	96	57.60	0.56	47	32	20.0
51 ± 2	168	57.70	0.35	53	44	20.2
51 ± 2	192	57.70	0.54	53	55	20.2
51 ± 2	216	55.40	0.30	59	57	20.2
51 ± 2	240	52.00	0.80	24	59	20.2
51 ± 2	264	56.00	0.72	24	57	20.2
74± 2	336	50.80	0.63	12	95	20.2
74± 2	360	56.00	0.43	19	110	20.4
74± 2	384	60.00	0.44	20	112	20.1
74± 2	408	61.00	0.59	22	106	20.0
74± 2	432	58.00	0.54	28	104	20.1
81 ± 2	504	62.00	0.64	27	102	19.6
81 ± 2	528	61.00	0.54	26	98	20.2
81 ± 2	552	62.00	0.72	28	103	19.5
81 ± 2	576	61.00	0.62	30	95	19.8
81 ± 2	600	59.00	0.74	23	132	19.6

Table 7.3 shows the results for all the samples taken at specific times with corresponding temperatures. The results indicate that the oil is definitely corrosive with regard to the presence of DBDS,

however, not corrosive with regard to copper windings corrosion. Table 7.3 shows the five main tests conducted on the oil samples. These include the DBDS concentration, furan concentration, interfacial tension, dielectric strength and water concentration. The water test produced the most significant changes from being 44 mg/Kg to 132 mg/Kg. The reason for the sudden increase in water will be discussed later in this section. Table 7.3 indicates that the DBDS concentration did not change significantly from the first day of testing to the last day, however, this is not the case when temperature changes are involved. Considering that DBDS is a sulphur compound found in the oil, one should expect that the concentration of DBDS would increase if the temperature is increasing. This will be discussed later. The presence of 0.74 ppm of Furans indicate that there is a mild to moderate deterioration of the insulation paper since the minimum concentration allowed is 2 ppm [87] before it is deemed to fail the Furans test. The presence of moderate furans indicates that the copper sulphide is being deposited on the insulation as previously proposed. The transformer failed the Dielectric Breakdown test [1] and the Interfacial Tension test [82] which have acceptable minimum values of 30 kV and 20 mN/m respectively. The Corrosive Sulphur test [38] showed the moderate tarnish of 2c for all samples however, the oil samples tested positive for being corrosive due to DBDS. The 2c results indicates a lavender, blue, claret red and silver colour was found on the copper strip. The transformer reached a maximum temperature of 81°C which was achieved by using external heating. This is the maximum temperature the transformer could possibly attain.

The next section describes the full kinetic analysis for the DBDS test results for all the temperatures in order to determine a reaction rate order and an activation energy. The rest of the chapter thereafter discusses the correlation between the test results and the DBDS concentration in transformer oil.

7.1.1 DBDS

The first temperature (T1) of 37 °C was obtained when the transformer was set at zero load. Figure 7.1 shows a plot of DBDS concentration against time. Experiments performed by Oweimreen et al. [88] and shown in Figure 7.2, identifies the concentration of DBDS to be approximately a decreasing function with time. However, our results as indicated in Figure 7.1 show a different behaviour. The DBDS concentration was first found to decrease until a minimum value was reached and thereafter began to increase. The DBDS concentration in the transformer at temperature 37 °C was a minimum of 42 ppm at 48 hours and a maximum of 57.60 ppm after 96 hours.

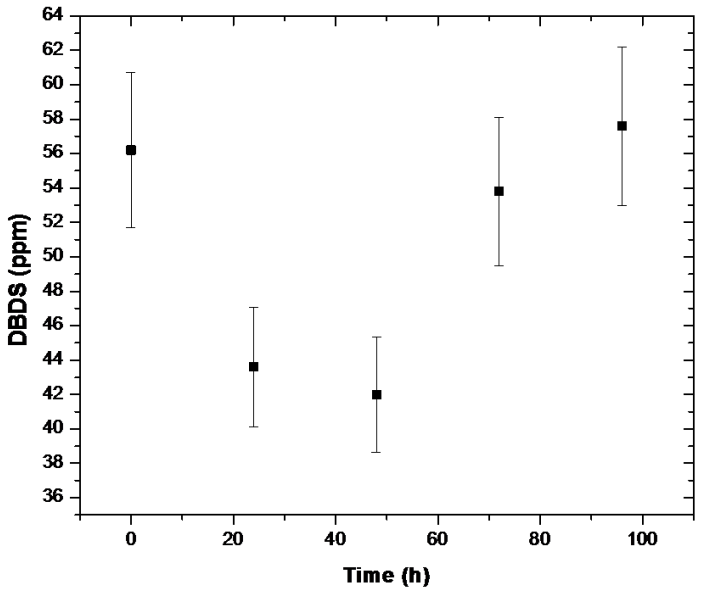

Figure 7.1: DBDS concentration versus time at 37°C ± 3°C.

It was established in Chapter 3, Section 3.1.5 on page 28 that DBDS is also found after copper sulphide is formed. This occurs since DBDS becomes the reactant and the result of the byproduct of the reaction with the copper and corrosive sulphur. This accounts for the increase in DBDS concentration as shown in Figure 7.1. The first three measurements (0 to 48 hours) would indicate that the reaction mechanisms of DBDS with copper which forms a DBDS-Cu complex can be identified when the DBDS concentration decreases. The last three data points (48 to 96 hours) in Figure 7.1 indicates the formation of copper sulphide and ultimately the increase in DBDS which is formed as a byproduct. The DBDS-Cu complex would have formed somewhere between 24 hours and 48 hours. Since this point was not obtained in the experiment, we approximate it to be the concentration of DBDS at 48 hours. The reaction in the transformer can be interpreted as DBDS reaching a specific minimum amount where the concentration is too low for further reaction with the copper and the DBDS-Cu complexes can thereafter form copper sulphide which increases the concentration of DBDS. The kinetic analysis of the DBDS concentration is therefore divided into a DBDS decreasing segment and a DBDS increasing segment.

The first step in analyzing the segmented results was to determine the rate order for each reaction

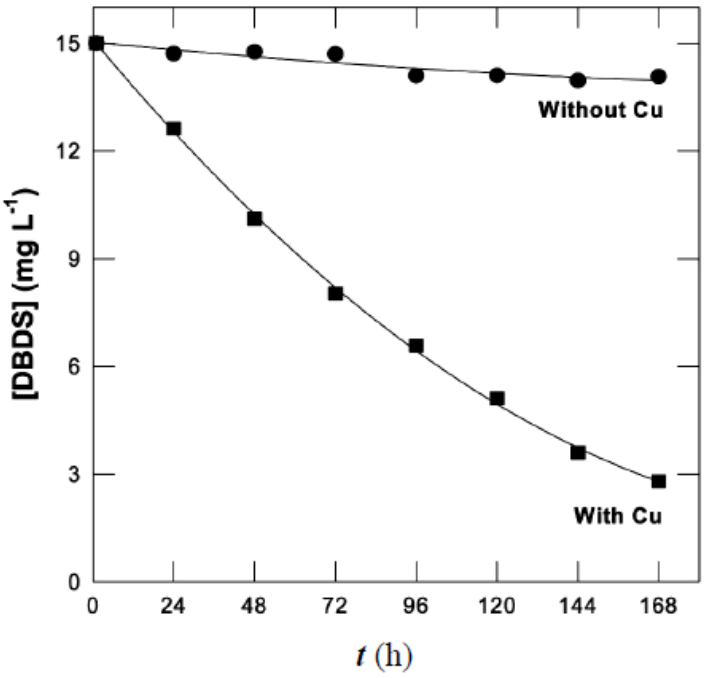

Figure 7.2: Experimental results displaying that DBDS decreases with time [88].

at each temperature. This was done using the methods discussed in the kinetics section of Chapter 4 .

The linear plot of the DBDS concentration versus the sampling hours produced a best correlation of 94.1% for T1. This corresponds to a second order reaction. The reaction produced a fit of $Y = 1.33 \times 10^{-4}X + 0.01825$ and this implied a rate constant (k) of (1.33 $\times$ 10 $^{-4}$ $\pm$ 4.79 $\times$ 10^{-5}) mol $^{-1}$.dm^{-3}h^{-1}. The second order reaction is illustrated in Figure 7.3.

The copper sulphide formation, (the increasing segment of the DBDS plot), produced the best linear fit correlation of 96.6% for the zero order plot. The DBDS increasing segment had a fit of $Y = 0.341X + 42.85$ and a rate constant of (0.341 ± 0.091) mol $^{-1}$.dm^{-3}h^{-1}. Figure 7.4 illustrates a larger image of the zero order plot which identifies that the copper sulphide concentration began to increase steadily after 48 hours of heating.

The same set of analysis was done for temperatures 51°C (T2), 74°C (T3), and 81°C (T4) to obtain a reaction rate order and rate constant.

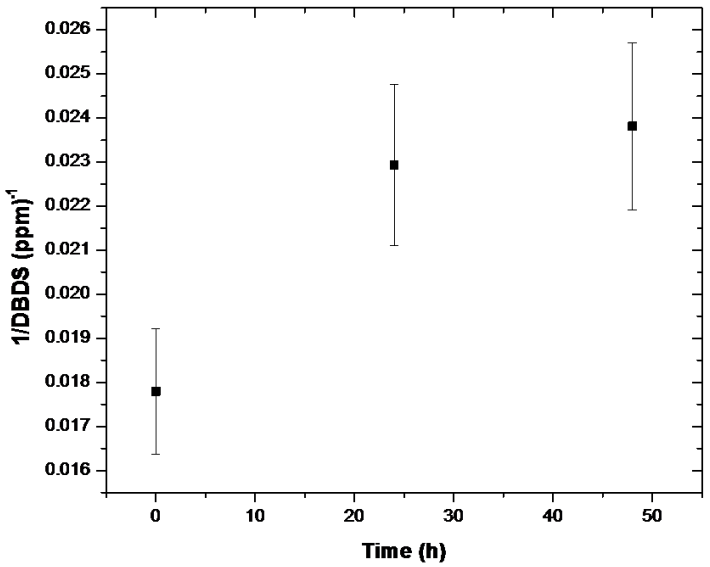

Figure 7.3: The DBDS concentration versus time for the second order reaction.

The linear plot of the DBDS concentration decreasing segment versus the sampling hours produced a best correlation of 87.2% for T2 which corresponds to a zero order reaction. The reaction produced a fit of $Y = -0.049X + 58.1$ and therefore a rate constant (k) of (0.049 ± 0.027) mol.dm^{-3}.

The DBDS increasing concentration plot for T2 produced a fit of $Y = -4.2 \times 10^{-6}X + 0.018$ and a best correlation of 14.2%. This correlation was for the second order fit and is regarded as a weak correlation. Due to the low correlation value, it was decided that this rate constant of ($4.2 \times 10^{-6} \pm 2.93 \times 10^{-5}$) mol $^{-1}$.dm^{-3}h^{-1} would not be used to calculate the activation energy.

The linear plot of DBDS decreasing concentration for T3 versus sampling hours produced the best correlation of 99.7% for the zero order reactions. The order of the reaction resulted in a rate constant of ($6.21 \times 10^{-5} \pm 7.73 \times 10^{-6}$) mol.dm^{-3}. The DBDS increasing segment plot produced a correlation of 67.1% for the zero order reaction. This resulted in a rate constant of (0.043 ± 0.047) mol.dm^{-3} for T3.

The kinetic analysis for the DBDS increasing segment for the T4 produced no reaction order. There is therefore no rate constant for the T4. The results for the T4 in Table 7.3 also display

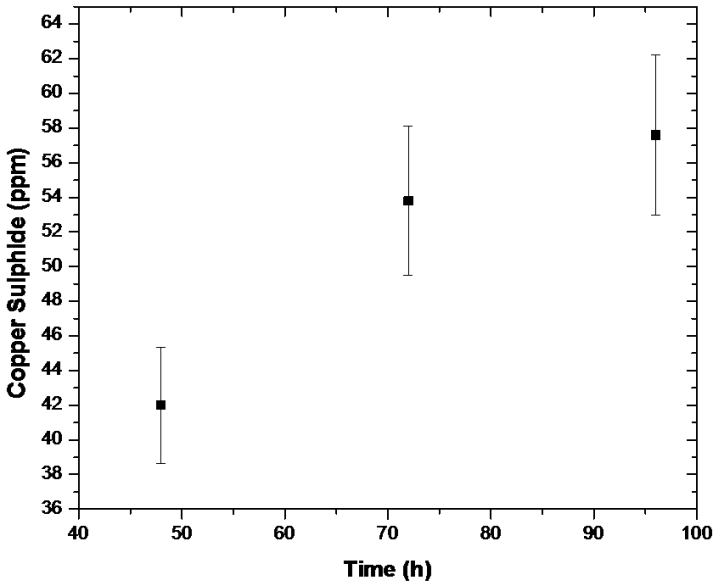

Figure 7.4: The copper sulphide concentration versus time for zero order.

that no rate constant can occur since the DBDS has reached saturation. The final temperature (T4) copper sulphide plot produced the best correlation for the zero order plot of 98.2%. This results in a rate constant of (0.063 ± 0.0120) mol.dm^{-3}. The results for the all the temperatures are summarized in Table 7.4.

7.1.2 Summary and Discussion of results for the DBDS reaction

The data from Oweimreen et al. [88] and the results from this experiment were found to be similar in that both data results showed a decreasing DBDS concentration as illustrated in Table 7.5. The biggest difference between the results is that the data from our experiment did not decrease after 48 hours of testing but increased and our initial concentration of DBDS was lower as compared to the 150 ppm concentration in the study by Oweimreen et al. [88]. Oweimreen et al. [88] identified visually from experiments that copper sulphide formed at temperatures of 100°C while our experiment showed, from Figure 7.4, that copper sulphide formed at low temperatures of 37°C.

The calculated rate constants show that the DBDS reactions occur in the transformer oil and fluctuated. The above results identify that the reaction of DBDS with the copper in the windings will

Table 7.4: The full analysis results of T1 to T4 where DBDS decr. is the DBDS decreasing concentration segment while DBDS incr. is the DBDS increasing concentration segment.

Temp °C	**Test**	**Order**	**Rate Constant** k	**Units**
37	DBDS decr.	Second	$(1.33 \times 10^{-4} \pm 4.78 \times 10^{-5})$	$\text{mol}^{-1}\text{dm}^{-3}.\text{h}^{-1}$
37	DBDS incr.	Zeroth	(0.341 ± 0.091)	mol.dm^{-3}
51	DBDS decr.	Zeroth	(0.049 ± 0.0273)	mol.dm^{-3}
51	DBDS incr.	None	-	-
74	DBDS decr.	Zeroth	$(6.21 \times 10^{-5} \pm 7.73 \times 10^{-6})$	mol.dm^{-3}
74	DBDS incr.	Zeroth	(0.043 ± 0.047)	mol.dm^{-3}
81	DBDS decr.	None	-	-
81	DBDS incr.	Zeroth	(0.063 ± 0.0120)	mol.dm^{-3}

Table 7.5: The experimental results of DBDS concentration in mg L^{-1} after *t* hours obtained by Oweimreen et al. [88].

Temperature (°C)	**24 h**	**48 h**	**72 h**	**96 h**	**120 h**
50	150.0	149.6	149.6	150.0	149.1
75	149.6	149.6	148.4	148.0	148.0
100	149.6	149.6	148.4	148.0	148.0
125	148.0	145.7	142.9	140.1	136.2
150	129.6	82.2	53.1	47.1	27.9

ultimately produce more DBDS. The decreasing concentration of DBDS plotted in Figure 7.3, agrees with the data of Oweimreen et al. [88]. However, Oweimreen et al. [88] results differ with ours in that the concentration of DBDS does not decrease indefinitely. The DBDS reaction can decrease since it is a second order reaction that is dependent on the initial concentrations of more than one reactant as compared to the other orders. The decrease in DBDS is therefore influenced by the actual concentration of DBDS and not by other mechanisms such as aging. The influence of the second order reaction was demonstrated when the initial concentration of 0.1ppm did not influence further formation or depletion of DBDS but a higher concentration of 56.2 ppm of DBDS did form more DBDS and eventually increase the amount of Cu_2S. The only problem with the situation of the depletion of DBDS is that it does not comply with the idea that DBDS increases

when non-reactive sulphur becomes reactive. This inconsistency in the assumption could be only in cases when DBDS is not actually present in the transformer since the initial concentration does influence the amount of deposition. The zero order reaction for the formation of copper sulphide in the transformer has also been identified as being possible since zero order reactions do not depend on the concentration of reactants but rather on time. The formation of DBDS and copper sulphide is therefore dependent on time since the DBDS-Cu complex after a prolonged period will covert to copper sulphide and DBDS.

The small rate constants found for T1 and T3 for the DBDS decreasing portion of the results indicate that the DBDS reaction with copper is slow in the transformer oil. The slow reactions are more prominent in the DBDS reactions than the Cu_2S formation reactions. The fastest reaction was found to be the formation of copper sulphide in T1. The copper sulphide rate order remained a first order throughout the experiment while the DBDS decreasing portion of the results began as a second order reaction and ended as a zero order reaction. This agrees with the assumptions made by Oweimreen et al. [88] who described that the rate of DBDS decreasing would eventually slow down and decrease in their orders since copper sulphide is forming. Oweimreen et al. [88] also refers to the point when the DBDS begins to increase as the "time of reflection point of the formation rate of Cu_2S " which agrees with our results that at a certain point of time the DBDS-Cu would convert to Cu_2S .

The initial rate constant of a lower concentration, in Oweimreen et al. [88], found that the DBDS reaction followed a zero order, however, at higher initial concentrations, rate constants began to become either first order or second order. This agrees with our experiment as the initial concentration was initially high which resulted in a second order reaction. However, assuming the final concentration of T1 was the initial concentration of T2, the concentration did decrease resulting in the order decreasing to zero order.

The lack of a rate constant at higher temperatures is due to the DBDS concentration reaching a saturation point at which DBDS can no longer react, however, the copper sulphide can form. If this experiment allowed more data points to be taken at a specific temperature, it would have been possible to fit our curves with higher order functions.

This experiment, as evident from Figure 7.1, illustrates that copper sulphide is formed and is indicated by the increase in DBDS. The initial experimental setup has also shown that DBDS cannot

react at low concentrations such as 0.1ppm. This supports the idea that a specific threshold is needed for DBDS reactions to occur. Temperature is also a major factor in the depletion of DBDS and the formation of copper sulphide. Previous studies have identified DBDS reactions to occur at temperatures above 150°C [35], however, we have shown that DBDS reactions can occur at temperature as low as 37°C in a transformer provided a significant concentration of DBDS is present.

The DBDS increasing segment rate constant results show an increase in the rate constant from the initial rate constant to the final rate constant. This increase in rate constants agree with literature [45], who identify that the higher the temperature, the greater the thermal energy and thus an acceleration in the reaction rate. The study by Amimoto et al. [45] also confirms that a threshold of DBDS is needed before copper sulphide is formed as illustrated in Figure 7.1.

The key points obtained from this study of the DBDS and copper sulphide reaction are as follows.

- The initial concentration of the DBDS in transformer oil will affect the formation and depletion of DBDS.
- The increase in DBDS identifies that copper sulphide has also been formed.
- At moderate temperatures, the DBDS rate constants begin to behave as a zero order reaction and are dependent only on concentration.
- The results obtained for this experiment is in agreement with work published in literature [35, 45, 88].
- Both copper sulphide and DBDS can react and form at temperatures lower than 100°C .
- At high temperatures, the DBDS concentration was found to reach equilibrium.

7.1.3 Activation Energy

The next set of analysis and a significant component of kinetic analysis is to determine the activation energy of the DBDS decreasing and the DBDS increasing mechanisms. The definition of activation energy, as previously mentioned, is the minimum energy required for a reaction to occur. To determine the activation energy, a ln k versus 1/T plot of the data in Table 7.4 is used.

The slope of the plot is substituted in the following equation :

$$\text{Slope} = \frac{\text{-E}_a}{\text{R}}, \tag{7.1}$$

where R is the universal gas constant of 8.314 J K $^{-1}$ mol $^{-1}$ from which the activation energy -E$_a$ can be extracted.

The activation energy for the DBDS reaction with copper, was found to be (-47.4 $\pm$ 8.5) KJmol^{-1}. The negative activation energy indicates the reaction is spontaneous and does not require heat to react. The minimum energy needed for the reaction to occur was therefore found to be (47.4 $\pm$ 8.5) KJmol^{-1}. This value is close to the literature value of Ren et al. [89] which is 43.7 KJmol^{-1}.

The activation energy for DBDS formation in transformer oil was found to be (-35.2 $\pm$ 3.82) KJmol^{-1}. The negative activation for the DBDS forming reaction also indicates that the reaction is spontaneous and that once the reaction has formed there is no way to reverse the reaction. The minimum energy required for the reaction to occur was found to be (35.2 $\pm$ 3.82) KJmol^{-1}. The is no literature pertaining to the increase in DBDS concentration and the activation energy of copper sulphide, however, there is literature data on the formation of vacancies on copper whose activation energy was found to be close to 44 KJmol^{-1} [90]. This activation energy describes the migration of copper ions from a copper surface. The theory behind the formation of copper sulphide had been linked directly to the migration of copper ions into the oil which forms copper sulphide. The activation energy was determined by Allen et al. [90] and supports the idea that copper sulphide is formed from the reaction of copper ions in the transformer oil. The activation energy of 44 KJmol^{-1} [90] compares favourably with our experimental activation energy of (35.2 $\pm$ 3.82) KJmol^{-1}.

7.1.4 Thermodynamic Properties

In this section, the activation parameters for the DBDS reaction and the copper sulphide formation were determined. These parameters included the activation enthalpy (ΔH), the activation entropy (ΔS) and the Gibbs free energy (ΔG) . The temperature for the thermodynamic study was the average of all corresponding temperatures for the rate constants which was found to be (327 $\pm$ 18.7)K and (329 $\pm$ 22.5) K for the DBDS decreasing reaction and the copper sulphide formation (DBDS increasing) reaction [54]. The errors for the activation parameters were estimated using error propagation. The activation enthalpy was found by substituting the activation energy into the

following equation:

$$\Delta H = E_a - RT. \tag{7.2}$$

The activation enthalpy for the DBDS decreasing reaction and DBDS formation reaction was found to be (44.6 $\pm$ 7.58) KJmol^{-1}and (34.4 $\pm$ 2.82)KJmol^{-1}.

The activation entropy was found by substituting the pre-exponential factor into the following equation:

$$\Delta S = RlnA - Rln(\frac{kT}{h}) - R. \tag{7.3}$$

The ln A (ln Pre-exponential factor) values for the DBDS reaction and the copper sulphide reaction were found to be (-26.01 $\pm$ 4.78) mol.dm^{-3} and (-14.75$\pm$ 1.36)mol.dm^{-3}. The activation entropy was found to be (-453 $\pm$ 19.3) Jmol^{-1}K^{-1} and (-360 $\pm$ 23) Jmol^{-1}K^{-1} for the DBDS decreasing reaction and the copper sulphide formation reaction. These low entropy values are likely since the reaction is not spontaneous and the probability of a reaction to take place is limited. The negative values for the activation energy found in this experiment agrees with theory [47], which claims that negative activation entropies indicate that the reaction is due to a particular mechanism and not a normal unimolecular reaction [54].

The last activation parameter, Gibbs free energy was found by substituting the above results into the following equation:

$$\Delta G = \Delta H - T\Delta S. \tag{7.4}$$

The Gibbs free energy was found to be (194 $\pm$ 13.6) Jmol^{-1}K^{-1} and (153 $\pm$ 14.4) Jmol^{-1}K^{-1} for both reactions.

The activation enthalpy of the DBDS reaction indicate that the reaction is not spontaneous since a large activation energy is required before the reaction can take place. The copper sulphide interaction also displayed the same characteristics, however, this reaction may occur on its own and cannot be prevented or stopped when the reaction occurs. The activation entropy describes the probability of the reaction to occur which is similar to the pre-exponential factor. The Gibbs free energy is the energy difference between the transition and ground state for a reaction. This factor demonstrates the energy required for a reaction to occur on a subatomic level. The findings show that both reactions occurred at different energies. The experimental data from our experiment cannot confirm that the reactions are a chemisorption reaction since the activation enthalpy is not in

the +200KJmol^{-1} range as shown by Ferral et al. [65]. This indicates that DBDS, with the current research, does not have the same properties as coverage and work function, as other molecules that react with surfaces.

7.1.5 The correlation between DBDS and other test results

In this section, we discuss the relationship between the concentration of DBDS on furans and water and the physical properties of the oil such as dielectric strength and interfacial tension.

Furan

The furan results are shown in Table 7.3. The experimental data results fluctuated for each temperature and therefore no kinetic analysis could be done on the data. The furan concentration versus time for each temperature is illustrated in Figure 7.5. These plots illustrate the fluctuations of data from the initial furan to final furan concentration for each temperature. However, the furan concentration did increase as the temperature was increased. The increase could be due to thermal stresses or the effect of contaminants.

The fluctuating furan concentration found in our experiment is similar to the results found in the by Lewand et al. [26]. The experimental data by Lewand et al. [26] as illustrated in Figure 7.6, also obtained furan concentration results that fluctuated with time. He reported that the increase in furans is attributed to overheating or a sudden temperature change that causes the solid insulation to degrade. The overall increase in Furans in both our data and the data obtained by Lewand et al. [26], is due to the furans being oxidized. The effect of contaminants on the solid insulation, as previously mentioned, would cause the formation of more furans, however, due to the fluctuations in the data, this is not conclusive.

The data obtained from this experiment can therefore be said to follow the typical data trends [26] for the deterioration of the insulation system and occurs due to thermal stresses in the transformer. It can therefore be concluded that there is no correlation between the DBDS concentration and the furan concentration. Further research is required to determine if the furans concentration can be used to estimate the development of copper sulphide.

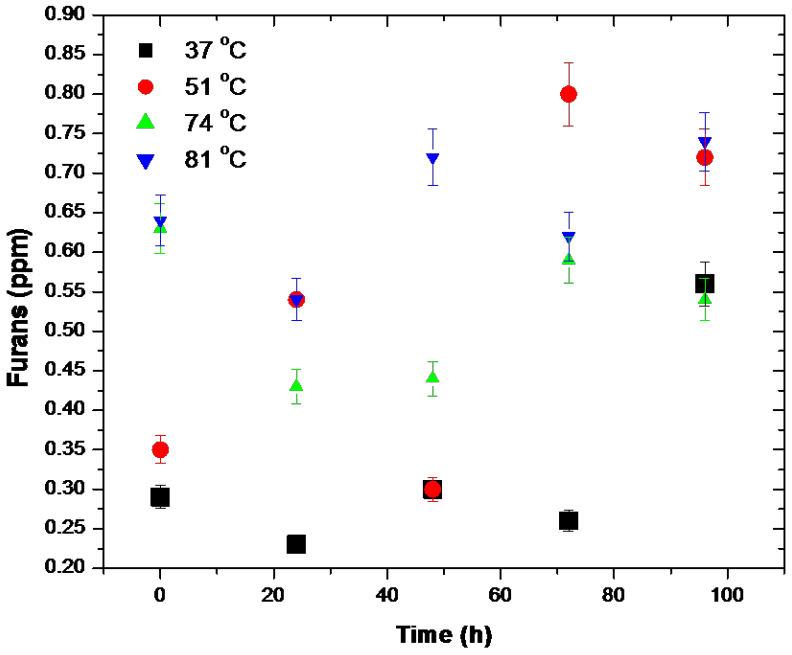

Figure 7.5: The furans versus time for each temperature in the period of 600 hours.

Dielectric Strength

The dielectric strength test monitored the influence of DBDS on the dielectric properties of transformer oils. The dielectric strength overall reaction was found to decrease which agrees with literature studies [92] that the dielectric strength should decrease with the increase in DBDS concentration. Research by Khan et al. [92] determined that the development of copper sulphide and DBDS would decrease the dielectric strength rapidly. The largest difference with our experimental data is that the dielectric strength measurements fluctuated within each temperature. The fluctuation of the data is illustrated in Figure 7.7 which shows that the dielectric strength does decrease, however, it also fluctuates within each temperature set. Since, the data by Verma et al. [91] did not fluctuate and was found to be constant, more literature analysis needs to be investigated to determine the accuracy of our experimental results. Results produced by Masanori et al. [93] also demonstrates that the data over a period of testing did decrease as illustrated in Figure 7.8. This decrease in the dielectric strength was due to the increase in the water concentration and the moisture content in the transformer. The increase in the water concentration is due to the oxidation of

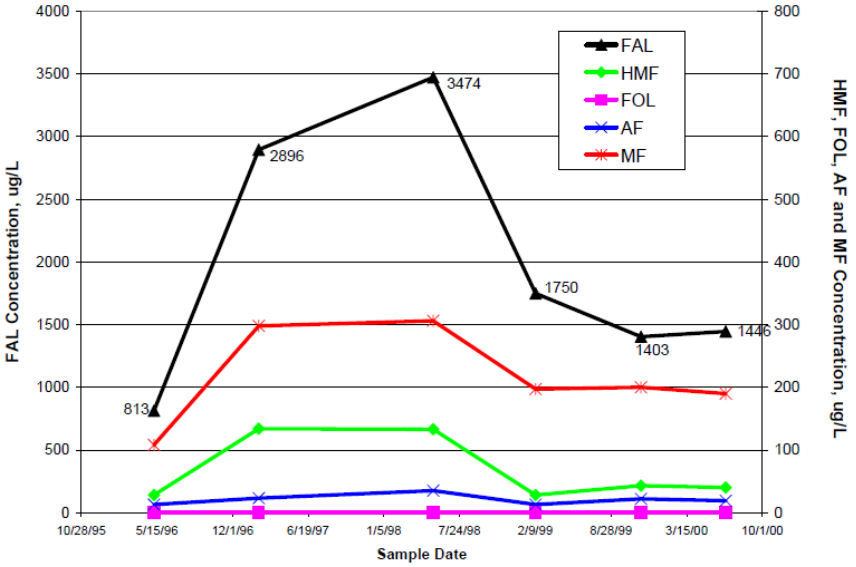

Figure 7.6: Experimental data by Lewand et al. [26] showing the fluctuating furan concentration versus sample date .

the water molecules which changes the dielectric strength. Masanori et al. [93] also concluded that the dielectric strength results were found to fluctuate similar to our data results. Our experimental data was highly unstable at higher temperatures which is a confirmation that thermal stresses are key factors in decreasing the dielectric strength.

The fluctuation in the data results indicate that the changes in the dielectric strength is not due to the presence of copper sulphide or DBDS but rather due to the deterioration of the insulation system and the changes in temperature. There is therefore no correlation, with current research, between the DBDS concentration and the dielectric strength.

Water

The correlation between the water content in the oil and the DBDS concentration was also investigated. The water content was seen to increase as the temperature was increased, however, it was also observed to fluctuate within each temperature. The total water content versus time for each temperature is shown in Figure 7.9. The fluctuation of the results in Figure 7.9 showed the fluctuation for each temperature with the final temperature producing the largest water content. Our results can be compared to the results obtained by Masanori et al. [93] which is illustrated in Figure 7.10. Masanori et al. [93] explain that after prolonged heating the water content will even-

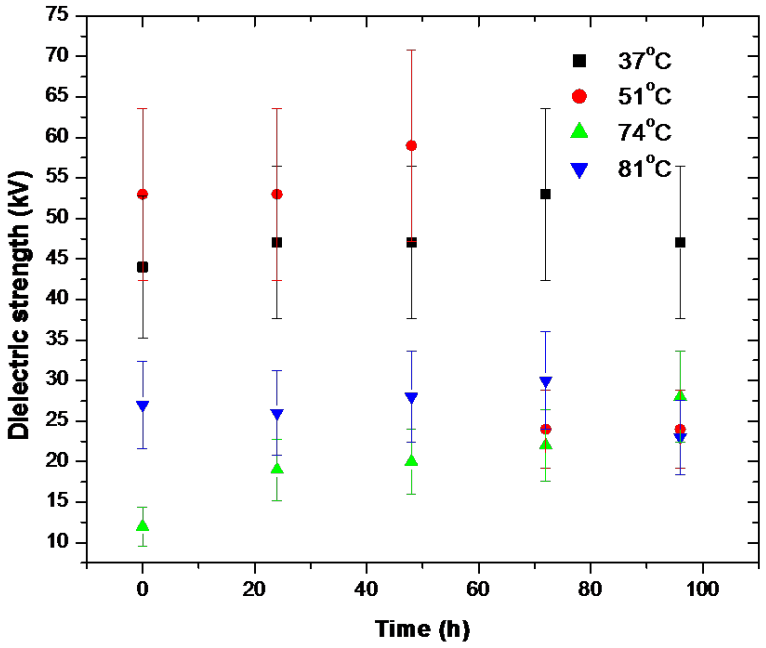

Figure 7.7: The dielectric strength versus time for each temperature in the period of 600 hours.

tually saturate. This differs from the results obtained in our experiment as the high temperature of 81 °C produced water content greater than at temperatures of 74 °C. However, higher temperature results would be needed in order to identify if saturation does take place.

The fluctuation in our experimental results imply that the change in the water content is due to heating and not due to the development of copper sulphide. At the end of Chapter 3, subsection 3.1.3, it was stated that a small amount of H_2O was produced and was negligible when copper sulphide is formed or when DBDS degrades . It is therefore possible from our data results that the copper sulphide did not increase the water content but rather oxidation is the cause for the further formation of water in transformer oil.

Interfacial Tension

The interfacial tension was the final chemical test performed to identify the condition of the oil and the effect DBDS concentration has on the interfacial tension. As observed from Table 7.3,

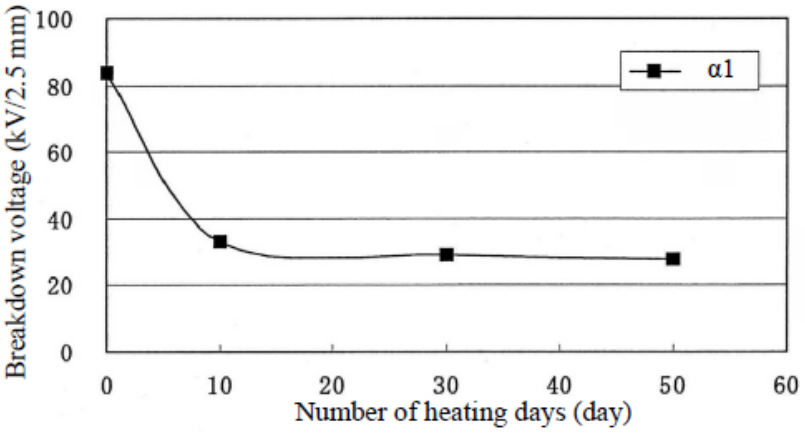

Figure 7.8: The dielectric strength versus time by Masanori et al [93].

the interfacial tension remains constant throughout the testing procedure with a small change from the initial to final interfacial tension. Our experimental data illustrated in Figure 7.11 agrees with the data produced by Masanori et al. [93]. Their data, as shown in Figure 7.12, identified that the interfacial tension reached saturation after a period of 10 days. The saturation occurred due to thermal stresses and not due to the formation of contaminants in the transformer oil. This saturated interfacial tension in both set of data identify that there is no correlation between the interfacial tension and the decrease or increase in DBDS concentration.

The chemical oil tests discussed in this section is typically used to determine the condition of the oil. Due to the lack of correlation between the DBDS concentration with the above mentioned oil test results, it can therefore be concluded that these tests cannot be used to determine the presence of copper sulphide.

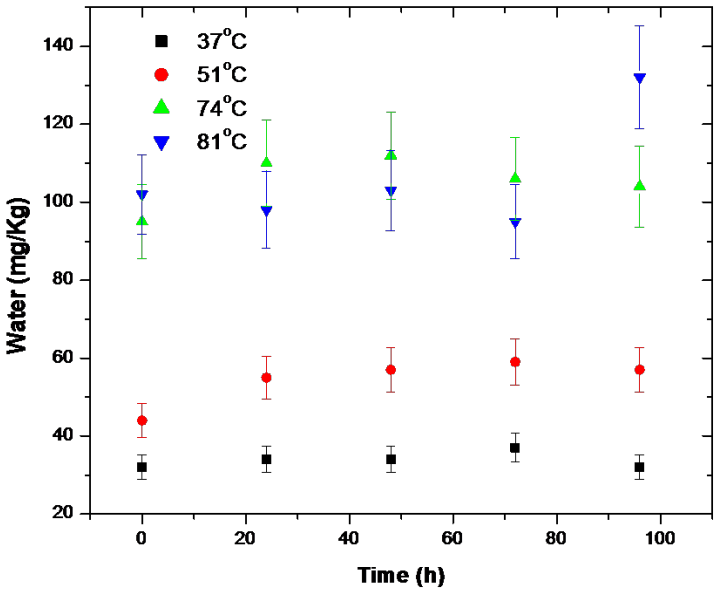

Figure 7.9: The water content versus time for our experimental data.

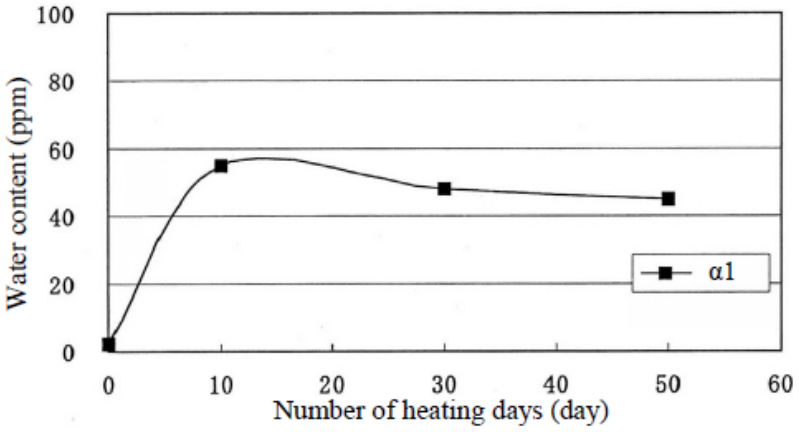

Figure 7.10: The water content versus time produced by Masanori et al. [93]

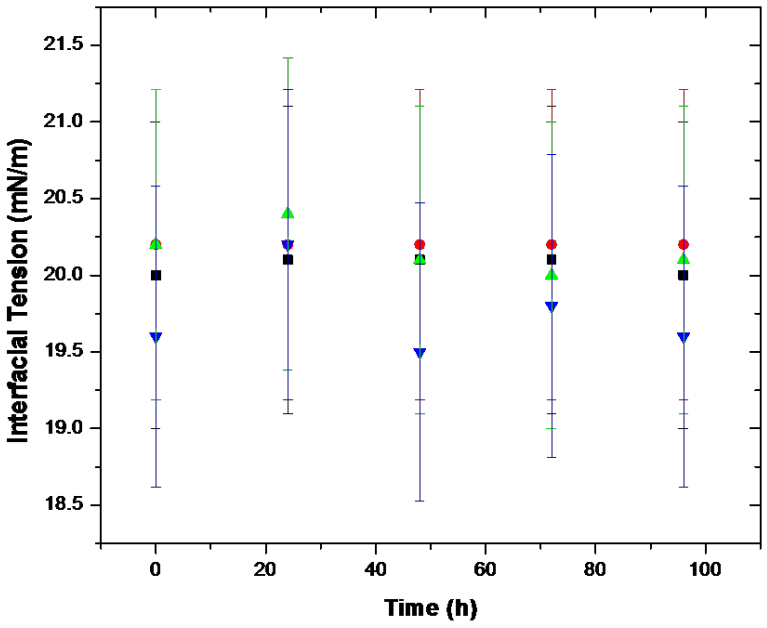

Figure 7.11: The interfacial tension versus time for our experimental data.

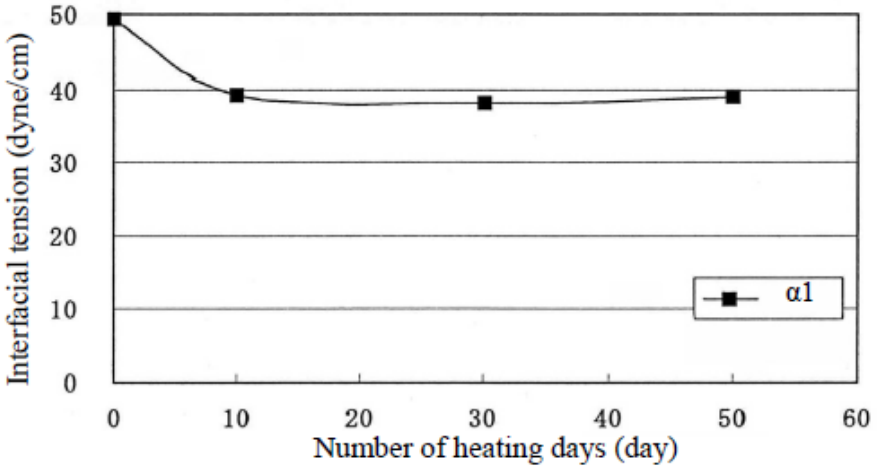

Figure 7.12: The interfacial tension versus time produced by Masanori et al. [93]

Chapter 8

Conclusion and Future Outlook

8.1 Conclusion

The objective of this study was to understand the role of corrosive sulphur in transformers and the formation of copper sulphide. The corrosive sulphur studied is DBDS which is known to degrade from a highly stable sulphur compound. The harmful effect of DBDS was found to lead to the formation of copper sulphide. The biggest problem with identifying the presence of copper sulphide is the fact that the copper sulphide deposits on a surface and the only way to accurately determine its presence is to dismantle the transformer. However, this study has identified through the analysis of DBDS concentration results that the copper sulphide form after the concentration of DBDS reaches a minimum point and thereafter the production of copper sulphide/DBDS begins to occur. Kinetic analysis of DBDS test results identified the order of reactions at specific temperatures. The activation energy of DBDS reacting with copper was found to be (47.4 $\pm$ 9) KJmol^{-1}. This result was found to be slightly different from other studies [89] since a study of oil samples from an active transformer was not done before. The high activation energy indicates that the DBDS can spontaneously react with copper and only when a large energy is reached. This provides a reassurance that transformers can last a longer time before corrosion takes place provided the amount of DBDS, which is put into the system as an additive, is controlled. The activation energy of copper sulphide formation (DBDS formation) was found to be (35.2 $\pm$ 3.82) KJmol^{-1}. This activation energy indicates that the reaction is spontaneous which complies with various literature that identify that copper sulphide is formed with no applied heat. This negative energy also implies that once copper sulphide is formed, it is difficult to slow the rate or prevent further interactions from occurring. This experimental study also indicated that DBDS and copper sulphide do not influence the properties of the transformer and transformer oil.

The main factor that contributes to the increase in the copper sulphide formation is temperature since the rate constant changed in each temperature. The initial concentration of DBDS also influenced the DBDS reacting with copper and the formation of copper sulphide. This was observed when the initial concentration of 0.1 ppm did not cause the DBDS to react with copper while a higher initial concentration of DBDS formed more DBDS.

The thermodynamics properties such as the activation enthalpy, activation entropy and Gibbs Free energy were also determined. The DBDS reaction with copper was found to have an activation enthalpy of (44.6 $\pm$ 7.58) KJmol^{-1}, while the activation entropy and Gibbs free energy were found to be (-453 $\pm$ 19.3) Jmol^{-1}K^{-1} and (194 $\pm$ 13.6) KJmol^{-1} respectively. These results indicated that a significant amount of energy is needed for a reaction to occur and the DBDS reaction is a spontaneous reaction. The copper sulphide formation reactions also produced a Gibbs free energy of (153 $\pm$ 14.4) KJmol^{-1}.

In conclusion, the investigation of corrosive sulphur in transformers has highlighted the key points of both DBDS reactions and copper sulphide reactions. There is a correlation between the DBDS and the formation of copper sulphide reactions. Kinetic analysis were done on these samples which provide a clear understanding of the influence of DBDS and copper sulphide on transformer oil.

8.2 Future Outlook

Failures of transformers have been linked to the windings becoming distorted and causing an overload of voltage in the transformers to occur [3]. The factors influencing the corrosive sulphur and copper sulphide formation have already been discussed, however, complete remedial procedures have not yet been investigated. Further research to identify the distortion mechanism that occurs between the copper sulphides and the copper conductors and to identify the severity of distortion needs to be investigated. Remedial procedures that could be implemented to prevent further distortion and failures of transformers also needs to be investigated.

Future research will attempt to utilize surface physics, which includes chemisorption, adsorption and deformation, to understand the mechanisms that occur between copper sulphide and copper conductors. Future work will also aim to understand the effectiveness of using a remedial procedures, such as passivators, in a system. Future research will also be geared to further understanding

of corrosive sulphur and copper sulphide in a liquid insulation (oil) and the solid insulation (paper) and to prevent further deposition of contaminants on the copper surface.

The current setup of the two transformers that were mentioned in this thesis will be used again in future research. The primary aim for future research is to run the current transformers until maximum copper sulphide deposition or until failure occurs. The copper conductors that contain the copper sulphide will be analyzed using various surface physics techniques. Another aim would be to model and simulate the factors influencing the formation, interaction and corrosion mechanism of copper sulphide. It is also envisaged that some of the data obtained from the experiments can be used to mathematically model the expected lifetime of transformers.

Research questions will include: understanding the effect of copper sulphide on the copper conductors and the effect of the magnetic and electric field on copper sulphide deposition. Using surface physics to determine if introducing a passivator would aid in preventing the distortion of the copper conductors. Can the distortion be rectified using chemisorption of sulphides on transition metals? Can effective rate equations be determined to prevent further failures of the transformers and the ultimate question is what actual effect does corrosive sulphur and copper sulphide have on the transformer oil and insulation system of the transformer?

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